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Gas chromatographic-mass spectrometric studies of shale oil and oil shale from the Rundle deposit, Queensland

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GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC STUDIES OF SHALE OIL AND OIL SHALE FROM THE RUNDLE DEPOSIT, QUEENSLAND

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ABSTRACT

Oil shale samples, from different stratigraphic levels in the oil shale deposit at Rundle, Queensland, were retorted by the Fischer Assay method (standard laboratory retort). The shale oils were chemically separated into 13 fractions and analysed by gas chromatography-mass spectrometry. Over 600 compounds were identified, including homologous series of linear alkanes, 2- and 3-methylalkanes, alkylcyclopentanes, alkylcyclohexanes, 1-, 2-, and 3-alkenes, alkylcyclohexenes, alkylcyclopentenes, 2-methyl-3-alkenes, alkylbenzenes, alkylnaphthalenes, 1-phenyl-4-alkenes, nitriles, methyl ketones, amides and carboxylic acids. Substituted benzenes, naphthalenes, polycyclic aromatic hydrocarbons, isoprenoid alkanes/alkenes, phenols, pyridines, quinolines and acridines were also identified. The oils are highly aliphatic in character (H/C = 1.6-1.7) with alkanes (approx. 30%), alkenes (approx. 20%), nitriles (approx. 12%) and methyl ketones (approx. 9%) being the most abundant components. The straight chain alkanes are the predominant compounds followed by the 1-alkenes. The carbon chain length distributions of the alkanes, nitriles and methyl ketones are bimodal indicating origins from both algal and higher-plant sources, with algal sources predominating. The pyrolytic origin of prominent and unusual components is discussed.

Oil shale from the Kerosene Creek seam (uppermost seam) was also retorted by the Lurgi-Ruhrgas process (commercial pilot plant) to yield light (b.p. 70-360^{o}C), middle (b.p. 200-480^{o}C) and heavy (b.p. 220-520^{o}C) oils. The Lurgi

oil fractions were chemically separated and analysed by the same procedure which was used for the Fischer Assay oils. The light, middle and heavy oils constituted 67%, 13% and 20%, respectively, of the total oil. The Lurgi oils are highly aliphatic in character (H/C = 1.5-1.6) with alkanes (15% in the light, middle and heavy oils) and alkenes (approx. 30% in the light, middle and heavy oils) being the most abundant components. The 1-alkenes are in greater concentration than the linear alkanes in the light oil and the ratio of 1-alkenes/ n-alkanes decreases as the carbon chain increases, whereas in the middle and heavy oils the n-alkanes are in greater concentration than the 1-alkenes. The concentration of short-chain aliphatic nitriles and methyl ketones (C_7 - C_{12}) is greater in the Lurgi oils than in the Fischer Assay oils. No amides were detected in the Lurgi oils.

The oil shale was also studied to examine the origin and maturation of the kerogen. An immature shale (Kerosene Creek seam; 13.2% total organic carbon (TOC)) and a carbonised oil shale (0.7% TOC) were extracted with organic solvents (benzene/methanol; 4:1 v/v) and then subjected to alkaline hydrolysis (10% KOH in methanol; 65°C) and stepwise alkaline potassium permanganate oxidation (80°C). Products were chemically fractionated and analysed by gas chromatography-mass spectrometry or direct-insertion mass spectrometry. The solvent extract (7% of total organic carbon (TOC)), from the Kerosene Creek oil shale, contained n-alkanes (C_{10} - C_{33}); acyclic isoprenoid alkanes; rearranged sterenes; pentacyclic triterpenoids; partially aromatised hydrocarbons with 2-5 rings; aliphatic, steroid and triterpenoid alcohols; mono-

carboxylic (C_6 - C_{30}) and α,ω-dicarboxylic acids (C_9 - C_{22}); amides and porphyrins. The solvent extract from the carbonised oil shale contained n-alkanes (C_{10} - C_{24}); acyclic isoprenoid alkanes; fully aromatised hydrocarbons with 2-5 rings; ketones; saturated (C_6 - C_{18}) and monounsaturated carboxylic acids (C_{14} - C_{18}); amides and porphyrins. No steroids, triterpenoids or α,ω-dicarboxylic acids were found in the solvent extract from the carbonised oil shale.

The alkaline hydrolysate (2% of TOC) from the Kerosene Creek oil shale, contained aliphatic monocarboxylic acids (C_5 - C_{28}), dicarboxylic acids (C_6 - C_{26}) and humic acids whereas the alkaline hydrolysate (2% of TOC) from the carbonised oil shale contained saturated acids (C_6 - C_{18}) and mono-unsaturated acids (C_{14} - C_{18}) but no humic acids. The permanganate oxidation of the Kerosene Creek oil shale produced predominantly α,ω-dicarboxylic acids (C_4 - C_{26}) and humic acids, whereas in the carbonised oil shale, only aromatic acids (mono- to tetracarboxylic) were produced upon oxidation. The permanganate oxidation reduced the TOC from 10.4 to 0.4% in the Kerosene Creek oil shale and from 0.5 to 0.1% in the carbonised oil shale.

This is the first detailed chemical analysis of shale oil and oil shale from an Australian deposit.

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INTRODUCTION

1. Oil shales as a liquid fuel source

A) Introduction to oil shales

Since 1945 the world has witnessed a remarkable technological and industrial expansion, made possible largely by bountiful and cheap supplies of petroleum. Coupled with the realization that petroleum resources are finite, the price increase in petroleum brought about by OPEC at the end of 1973 has made necessary a complete new assessment of the utilization of all natural energy resources. It has also been apparent that indigenous supplies of cheap crude in Australia may run down in the near future. In the light of this, the reserves of oil shale stand out as a very important source of substitutes for petroleum. The oil shale industry is not new. Before and during World War II, imbalance in distribution of raw materials led to the development of oil shale industries, which proved to be short lived, because the industry could not compete economically with the recovery of petroleum in peacetime.

It has been estimated that the total world reserves of shale oil are 30×10^{12} barrels of which 2% or 600×10^{9} barrels are available for present-day exploitation. Of this, the Green River formation in the United States contains an estimated 700 billion barrels of economically recoverable synthetic crude oil (Yen and Chilingarian, 1976). In Australia, large deposits of oil shale occur in Queensland (Figure 1) and reserves of in-situ shale oil in the Rundle, Julia Creek, Condor, Duaringa, Stuart and Nagoorin deposits have been estimated to be 2.6, 1.5, 8.4, 3.7, 2.5 and 2.6

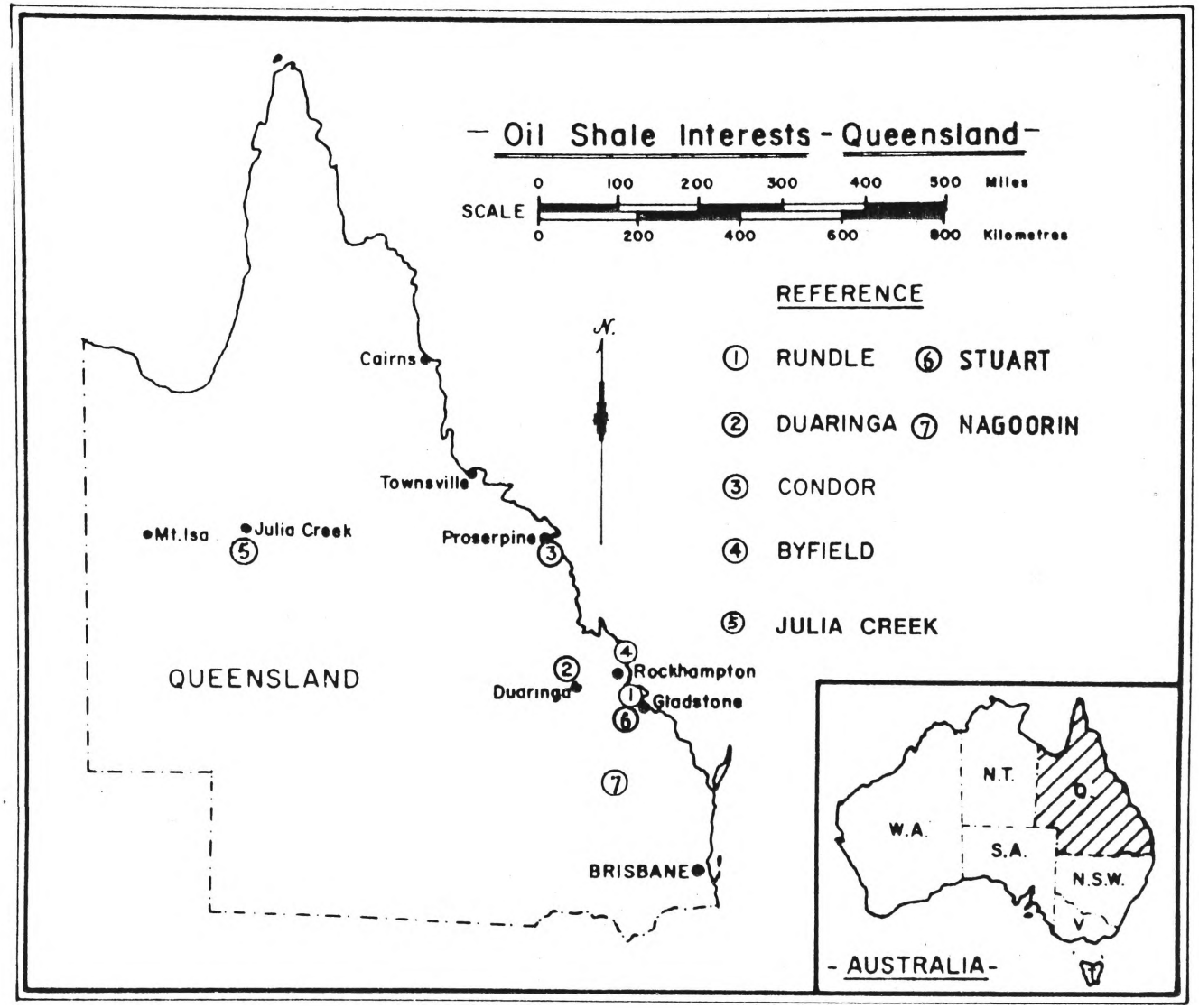


Figure 1. Oil shale deposits in Queensland

billion barrels respectively (Southern Pacific Petroleum NL, 1981). Other deposits in Queensland are under investigation.

B) Definition

Oil shale can be classified as composites of tightly bound organic and inorganic materials. The ratio of organics to inorganics rarely exceeds 1 : 4. The inorganics include quartz, feldspars, clays, carbonates, pyrites and other minerals whereas the organics can be divided into a bitumen fraction, (soluble in organic solvents) constituting anything up to 20% of the organic material, and kerogen (insoluble in organic solvents). Upon heating the shale (500 - 600^{o}C) the kerogen dissociates into smaller molecules producing crude oil. The composition of the kerogen depends on its origin. All oil shales appear to have been deposited in shallow lakes, marshes or areas which support a dense algal biota, the latter being a possible source for the shale-bound organic material.

C) Origin and formation of oil shales

(i) Likely materials in kerogen formation

Many substances have been suggested as the source material of oil shale kerogen, including resins, spores, lignin, algae, bitumen and animal remains. It is now generally agreed, that some, if not many, oil shales owe their origin to algal growth. Although algae may have been the main contributor, it is undeniable that a variety of miscellaneous detrital materials have been associated with depositions. Wind-borne plant debris is important in some deposits, and, in all cases, the effects of microbial action

cannot be ignored.

Because the concensus is that algal residues play a major role in kerogen formation, it is useful to examine the lipid types likely to have been involved. The main chemical compounds are esters of fatty acids and hydrocarbons. Fatty acids are present in nearly all life forms and occur in large quantities. Suitable members of the group possess sufficient chemical reactivity to polymerize to hard, insoluble and inert material similar to kerogen. Polyene acids, so characteristic of algal fats, are highly reactive and Cane (1967) has suggested several mechanisms for the formation of kerogen-like polymers. The algal classes most likely to contribute to kerogen formation are members of the Chlorophyceae (green algae) or Cyanophyceae (blue-green algae).

The individual types of organic matter found in sedimentary rocks are termed macerals and are usually defined within one of three groups inertinite, vitrinite or exinite. Inertinite and vitrinite are generally rare in oil shales whereas most forms of organic matter in oil shale are included within the exinite group of macerals as they are largely algal in origin (alginite) with a lesser contribution from spores, pollen and cuticle of higher land plants (sporinite, cutinite).

According to Hutton (1981), exinite can be divided into a number of groups:

a) Sporinite - spores and pollens

b) Cutinite - cuticles or waxy outer layers from leaves and stems

c) Resinite - resins, fats, waxes and oils

d) Alginite which can be subdivided into two groups:

   1) alginite A - discrete algal bodies which are

either elliptical or disc shaped and which form the characteristic algal components of torbanite, tasmanite and kukersite. All recognised genera belong to the Chlorophyceae (green algae).

2) alginite B - finely bonded lamellar alginite intimately interbedded with mineral matter in well laminated deposits such as Rundle and Green River formation. The genera belong to either Cyanophyceae (blue-green algae) or Chlorophyceae (Hutton et al., 1980).

(ii) Types of oil shales

A number of oil shales have been classified (Hutton et al., 1980) and these are as follows:

a) Torbanite. This is a high grade oil shale composed of abundant alginite A related to the present day green alga Botyrococcus braunii and is synonymous with boghead coal or kerosene shale. The majority of torbanites are lenticular bodies occurring close to, or bounded by, coal horizons. Torbanite occurs in the Ermelo district in Transvaal, South Africa, in the Midlothian and West Lothian countries, Scotland, and in the Sydney Basin of New South Wales (e.g. Glen Davis) in Australia. Torbanites are characterized by a minor contribution from mineral matter and, hence, are very rich in organic material. The colour of torbanite is shiny black with algal colonies exhibiting intense fluorescence under blue light/U.V. irradiation with colours ranging from green through yellow to orange. Shale oil yields commonly range between 250 and 500 litres per tonne of shale. The reserves of torbanite comprise only a small proportion of Australia's total oil shale reserves.

b) Tasmanite. This shale has, as its main organic constituent, alginite A, derived from the remains of the

unicellular marine alga Tasmanites and is found in Tasmania. The Tasmanian deposit along the Mersey River produced oil yields of 45 to 130 litres per tonne. Tasmanites largely consist of compressed algal discs which occur in a fine-grained groundmass of clay minerals and quartz. The ore reserves are estimated to be 25 x 10^6 tonnes (Turner, 1965).

c) Lamosite. Lamosites are well laminated oil shales containing abundant alginite B and minor alginite A. The world's largest resources of oil shale are lamosites and this includes the Green River formation and the Rundle deposit in Queensland. Alginite B, is the dominant exinite maceral in lamosite and it occurs with minor vitrinite, Botyrococcus related alginite A and traces of sporinite. A feature of lamosites is the lipid-rich frame of the biomass which envelopes mineral grains and then coalesces to form an intimate association of organic matter with mineral matter. The nature of this association may indicate an algal mat origin. Lamosites are commonly associated with hypersaline environments as in the case of the Green River formation.

d) Mixed oil shale. These shales contain a mixed assemblage of organic matter comprising vitrinite, alginite B derived from dinoflagellates, alginite A (Tasmanites), sporinite and resinite derived from higher plants. The Toolebuc formation in Queensland, which includes Julia Creek deposit, has two seams of mixed oil shale with an average yield of oil at 60 litres per tonne.

e) Kukersite. This shale is of marine origin, containing alginite A derived from algae referable to Gloeocapsomorpha.

(iii) Formation of oil shales

The principal environments for oil shale deposition are:

a) large lakes. Some of the richest, most extensive and thickest deposits of oil shales have been deposited from this environment, e.g. the Green River formation.

b) shallow seas on continental platforms and shelves. The platform shales are thin, only a few feet to a few tens of feet thick with yields of less than 135 litres of oil per tonne. They are mostly of the siliceous type, black in colour and include the shales of Cambrian age in northern Europe, Devonian age in eastern and central North America, Permian age in southern Brazil and Argentina and Jurassic age in Europe and Alaska.

c) small lakes, bogs and lagoons associated with coal-producing swamps. These oil shale deposits are relatively small, although many are high grade, yielding up to 190 litres of oil per tonne of rock.

Experimental evidence indicates that the formation of oil shales probably did not occur at temperatures in excess of 150^{o}C and that changes in chemical composition commenced from the moment of deposition. With ageing of the algal mats, polymerization and biochemical decay would cause a decrease in chemical unsaturation, whereas proteins and carbohydrates would be removed under aerobic and anaerobic conditions. Later under anaerobic conditions, polyene fatty acids would lose carboxylic groups by condensation or bacterial attack. Bacteria can also modify structures, increase the chain length of organic molecules and destroy

or hydrogenate double bonds. Throughout all these changes, more stable forms of matter are created at the expense of the less stable ones. The effect of the maturation is a uniform decrease in oxygen of the protokerogen and the generation of an essentially hydrocarbon structure. An intermediate phase allows increase in molecular cross-linking and development of structure whereas the geological burial period serves to mature the chemistry. The above processes result in the final product which is a tough inert organic polymer called kerogen. Cane (1971) suggests that pressure alone would have little effect on the diagenesis of organic matter.

D) Recovery methods

(i) Extraction of oil from oil shales

The organic matter in oil shale contains both bitumen and kerogen. The bitumen is only a minor portion of the organic material and is soluble in organic solvents whereas the bulk of the organic material is composed of kerogen which is insoluble. Several approaches may be used to separate the organic material from the inorganic matrix:

1) drastically break the bonds of the organic material,
2) mildly degrade the organics, and
3) remove the inorganics while keeping the organic material intact.

The first approach is used in industry and is called retorting.

(a) Surface retorting

In the case of surface retorting, the shale is mined, crushed and conveyed to a retorter, where the shale

is heated to about 500°C. As a result, the chemical bonds are broken and the liberated compounds, in the gaseous state, are collected and condensed to produce crude oil. This crude oil is then hydrotreated and refined into the final products. The above-ground retorts now considered for commercial application can be grouped in three categories:

1) Retorts heated by a flow of internal combustion gases through a fixed or moving bed of crushed oil shale. Examples include the NTU retort (Nevada - Texas - Utah), the gas combustion retort, the Paraho direct system and the Union A. Such retorts produce a spent shale low in residual carbon and a low-Btu gas. Their thermal efficiencies are high, because energy is recovered from the retorted shale. However, shale oil recovery efficiencies are only 80 - 90% of that obtained by direct pyrolysis at 500°C (standard Fischer Assay procedure).

2) The second category consists of indirectly heated retorts that contact the crushed oil shale with flowing gases heated outside the retort. This group includes the Union B, the Paraho indirect, Petrosix and Superior retorts. Several others are under development including the Texaco catalytic cracker and the Union SGR and SGR3 designs. This group of retorts leaves a carbon deposit on the spent shale but produces a high Btu gas. Thermal efficiencies are relatively low, because energy is not recovered from the residual carbons, but oil recovery is high (90 - 100% of Fischer Assay).

3) In this third category, heat is transferred by solid-to-solid contact in a mixing system. Examples include the Tosco II, the Lurgi-Ruhrgas (L-R) and a Soviet design. Tosco II and L-R produce high oil yields (100% of Fischer Assay) and a high Btu gas. The L-R system uses a bleed stream of hot spent shale for solid-to-solid contact, while Tosco II cycles heated ceramic balls through the retort with oil shale feed. Both types of retorts are externally heated and both systems provide an effective disengagement of gases and solids.

These systems have several limiting factors in common.

1) Present retorting methods all require an expenditure of thermal energy, which may be supplied by electrical arc, gas combustion, or other energy sources. Even in-place retorting methods still require expenditure of a considerable fraction of the energy contained in the fuels released from oil shales. This diminishes the net energy production.

2) Retorting is not an efficient method for the liberation of organic material locked in oil shale. At best, 70% of the organic material can be removed using existing technology. The remaining 30% is closely tied to the inorganic matrix, and therefore cannot be extracted.

3) Retorting produces large volumes of waste rock, which undergoes a volume increase (about 10%) during processing. These large volumes of spent shale present an important disposal problem.

4) Retorting results in the formation of large amounts of carcinogenic compounds such as polyaromatic hydrocarbons

which pose a potential health hazard.

5) At high temperatures, dehydrogenation and aromatisation of hydrocarbons occurs. As a consequence, large amounts of hydrogen have to be used during subsequent refining processes.

6) Shale for surface retorting must be mined and transported to the processing plant, which may cause environmental damage in addition to transport expense.

Therefore there is a need for research and development of economically and environmentally more favourable methods to recover oil from oil shales.

(b) In-situ processing

Since mining, crushing and aboveground retorting make up a substantial portion of the cost of producing shale oil, in-situ retorting has received some attention as a possible means of reducing the cost of shale oil production. This process has a number of advantages. It may be applicable to deposits of various thicknesses, grades and amounts of overburden that are not readily amenable to mining. Also it eliminates the necessity of disposing of large quantities of spent shale. A disadvantage in that there is a possibility of groundwater leaching the soluble retorting products left underground. However, in-situ retorting is still in the very early stages of development.

One of the simpler techniques consists of drilling wells having a predetermined pattern into the oil shale formation, creating permeability among the wells if naturally occurring permeability is low, igniting the shale in one or

more of the wells, pumping compressed air down the ignition well to support combustion of some of the oil shale, forcing the hot combustion gases through the oil shale to convert the solid organic matter in it to oil and recovering the oil. One aspect that has received some attention is how to obtain the necessary permeability. Some of the methods which have been examined are as follows:

1) Fracturing. Fracturing can be achieved through the use of explosives both conventional or nuclear. In conventional fracturing a series of wells are drilled and explosives are placed at the bottom of each well. The degree of fracturing resulting from detonation of these explosives is a function of the explosive power, rock strength and depth of well. It has been suggested that nuclear explosives could be used in a similar manner.

2) Injection of fluids. Hot gases, water and other fluids can be injected into the wells and forced through the fractures. These fluids are able to expand the width of the fractures and push the fractures deeper into the shale bed, i.e. extend the fractures.

3) Fluid migration. If hot gases are passed through the rock bed, liberation of organic compounds may occur. The latter may then flow along with the gases to a producing well where they can be brought to the surface.

Apart from the above in-situ processes another type has been considered as an alternative. This involves biological agents.

4) Biochemical recovery. Biodegradation and

biodisintegration of the inorganic components in the oil shale matrix has been considered to separate the inorganic matrix from the organic material. The organic-inorganic linkages can be disrupted by microorganisms to cause the organic components to separate. The oil shales of the Green River formation, for example, contain large amounts (approx. 50%) of acid-soluble carbonates, which are susceptible to degradation by acid-producing bacteria. The erosion of oil shale minerals by bacteria may lead to the partial release of bound kerogens and facilitate their subsequent production. Extensive research on biochemical recovery methods is being conducted at the University of Southern California under the direction of Dr. Yen. The disadvantages of bioleaching are that large amounts of water are required and as well as the successful generation of a sufficent amount of bacteria to tolerate the chemical and thermal environments at depths of 300 metres.

(c) Solvent processing. Solvent processing consists of heating the shale in the presence of a solvent at low temperatures (320 - 430^{o}C) with or without a high partial pressure of hydrogen. Separation of mineral matter from products must be by gravity flow, sedimentation or filtration. Published work does indicate that up to 95 - 100% of the organic matter (equivalent to 141 - 148% of Fischer Assay) can be recovered by solvent extraction methods. Recent patent literature shows liquid yields of 110 - 120% of Fischer Assay where steam is flowed at low temperatures (430 - 450^{o}C) over beds of shale. Up to 90% of Fischer Assay

has been obtained at 290°C after 18 to 20 days. Advantages of solvent extraction are simpler and more rapid heat transfer, higher yield of liquid and less refractory nature of liquid.

(ii) Conversion of shale oil to liquid fuels

Before raw shale oil can be introduced into conventional refining processess, it must be upgraded into a synthetic crude. This is necessary to reduce the high concentration of impurities such as nitrogen, sulphur, oxygen and trace elements, especially arsenic. The removal of arsenic is normally carried out in guard case reactors prior to introduction to the hydrotreater so that arsenic will not poison the catalysts. Figure 2 shows an overall block diagram for refining shale oil to petroleum. Nitrogen is the main and most difficult contaminant to be removed. Hydrodenitrogenation is accompanied by complete desulphurization, olefin saturation and substantial aromatic saturation. Following adequate hydrotreatment, upgraded shale oil may be processed by hydrocracking, catalytic cracking or catalytic reforming in the same way as high quality petroleum stocks.

2. Geology of the Rundle oil shale deposit

A) History of the deposit

Tertiary oil shale was discovered about 20km northwest of Gladstone, Central Queensland, during dredging of The Narrows Channel in the late nineteenth century (Ball, 1914). Fuel shortages during World War II led the Queensland Mines Department to drill 15 holes with diamond drills between 1914 and 1943 (Ball, 1946). It was concluded that

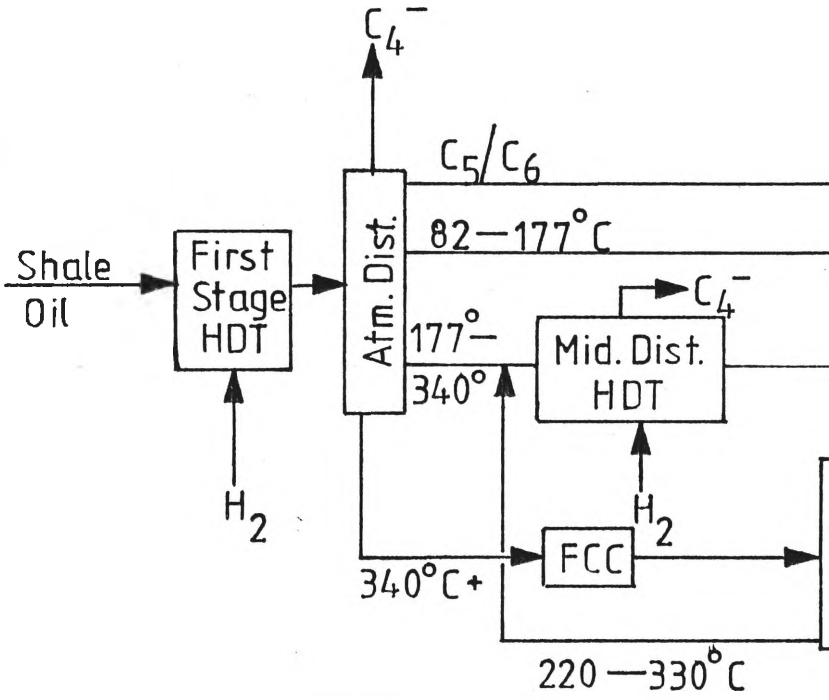
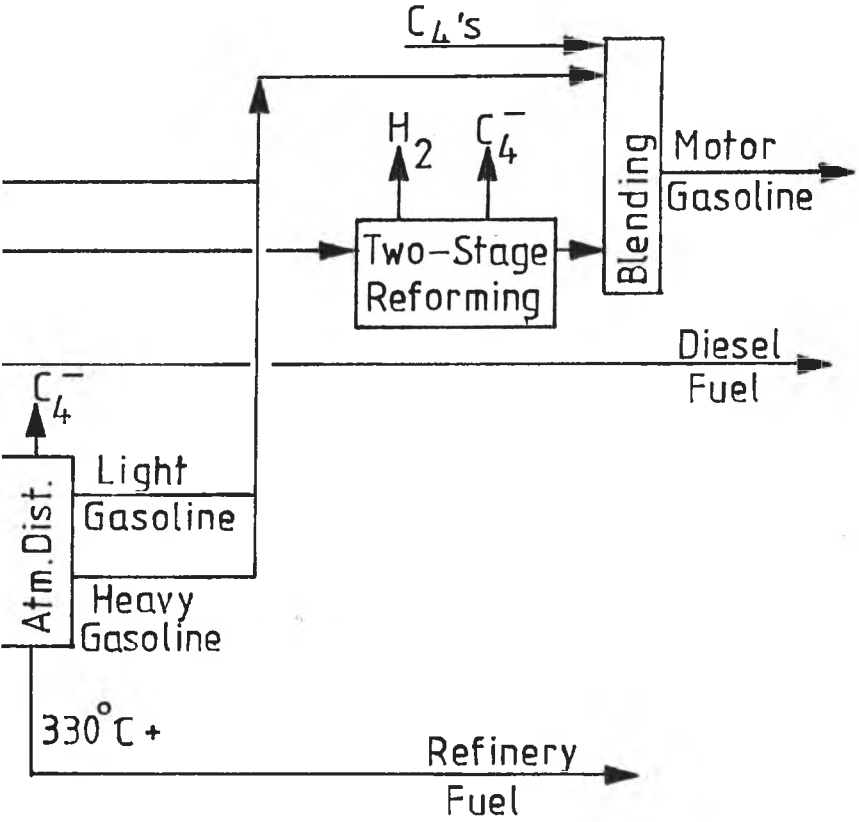


Figure 2. Schematic diagram for



refining shale oil to petroleum

within an area of about 3100 hectares, there was more than 1000 million tonnes of oil shale of which 630 million tonnes could yield more than 67 litres of shale oil per tonne. After World War II, cheap Middle East crude oil became available and this forced the oil shale industry to close. Southern Pacific Petroleum and Central Pacific Petroleum began investigating the area in 1974, and by 1980 drillings had outlined two separate, but similar, oil shale deposits. In-situ shale oil reserves have been calculated to be 2.2 billion barrels for the Rundle deposit and greater than 2 billion barrels for the Stuart deposit. Lindner and Dixon (1976) used the results of early drilling data to report on the geology of the Rundle deposit.

B) Geography

The Rundle oil shale deposit lies on a flat, north-trending valley flanked by Curtis Island and the Pacific Ocean to the east and steep hills of the Rundle and Mount Larcom ranges on the mainland to the west. Curtis Island is separated from the mainland by a shallow channel (The Narrows) only 300 metres wide at Ramsay Crossing. The coastline is fringed with mangroves along a tidal flat. The jagged peak of Mount Larcom is the highest point (632m). The climate is subtropical and most of the average annual rainfall of 860 mm occurs between December and March.

C) Geology

(i) Regional

The Gladstone and Narrows areas of Central Queensland are underlain by the Carboniferous Curtis Island

Group. The Group consists of deepwater sedimentary rocks which were uplifted and folded during the Late Permian. During the Upper Cretaceous, trachyte and rhyolite plugs (Mount Larcom) intruded the Curtis Island Group. A lacustrine system developed in the Early Tertiary and sedimentary rocks accumulated within a graben in The Narrows area. Subsidence and deposition produced a sedimentary pile more than 1000 metres thick that was later invaded by olivine dolerite.

(ii) Surface

The Tertiary sequence in The Narrows Graben is unconformably overlain by an extensive cover of alluvium comprised of gravel, sand and clay. Sand and gravel are most extensive in the south and range up to 25 metres in thickness. Outcrops of the Tertiary sedimentary rocks are sparse and confined to creek beds and along the intertidal zone of The Narrows Channel. They are deeply weathered and consist of kaolinized shale and claystone commonly off-white with patchy dark red-brown oxidation colours. Most of the outcrops are of the Brick Kiln and Kerosene Creek seams. Fresh oil shale is exposed at the confluence of Kerosene and Munduran Creeks. Small scale faulting is evident in a number of places in creek exposures. There is a reverse fault in weathered shale in Kerosene Creek which has a throw of about 1 metre.

(iii) Stratigraphy

Stratigraphic subdivision of the Tertiary sequence within The Narrows Graben was made on the basis of drill hole information. Three formation names have been proposed for the sequence: Worthington (the oldest), Rundle and Curlew. The Rundle formation is the most prospective

and consists of a kerogen-rich sequence that can be subdivided into the following stratigraphic levels (Figure 3) (Henstridge and Missen, 1981).

Rundle formation

1) Kerosene Creek seam. This seam is the uppermost oil shale seam of the Rundle formation and is dominantly composed of oil shale with minor persistent claystone and carbonaceous shale/oil shale beds. It has the highest average oil yield (121 litres per tonne) within the graben. The average thickness is 43 metres and the calculated oil reserve of the seam is 170 x 10^6 barrels. The seam is not continuous through the graben - it occurs as three separate, but correlatable seams, two in the Rundle deposit and one in the Stuart deposit. The oil shale is generally dark to moderate yellowish-brown to olive-brown. In the central part of the Rundle deposit, there is a persistent claystone bed from 5 to 10 metres below the top of the seam. Northwards, a claystone bed thickens and separates the Kerosene Creek seam into two distinct oil shale beds. In the southern part of the graben, the seam's oil yield increases and claystone is less significant.

2) Telegraph Creek unit. This seam consists of dark greenish-grey claystone with minor oil shale interbeds. The claystone ranges from soft to moderately hard. Two oil shale beds (0.5 to 2 metres thick) exist in the central part of the unit and are generally 4 to 6 metres apart. There is a very persistent oil shale "marker bed" (up to 10 metres thick) about 10 to 15 metres below the top of the unit and forms the only outcrop of non weathered oil shale within The Narrows Graben.

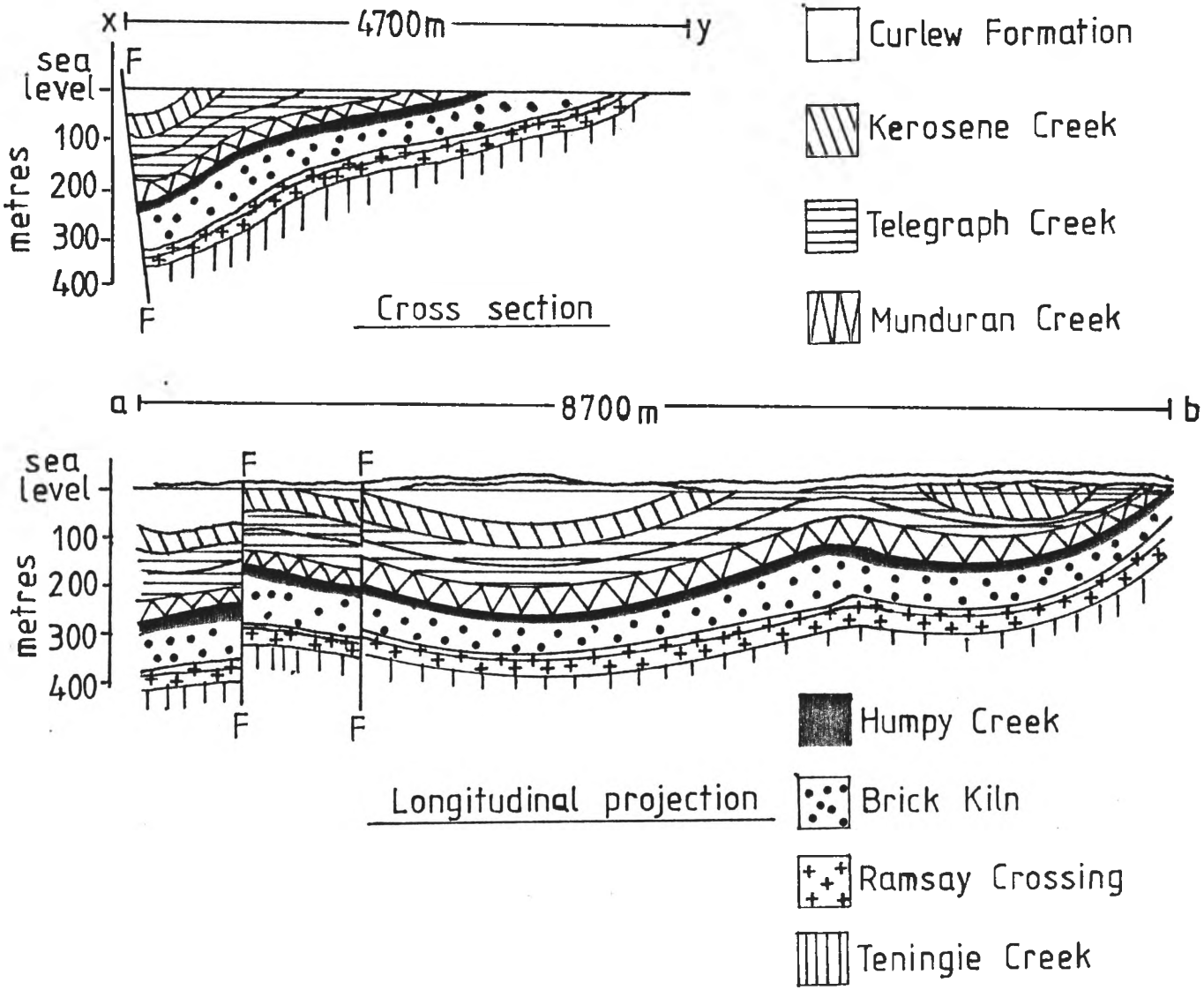


Figure 3. Cross-sectional and longitudinal projection of the Rundle deposit as indicated in Figure 4.

In the basal 10 metres of the unit, there are brown oil shale patches and thin beds producing a lithological gradation to oil shale into the underlying Munduran Creek. The average thickness of the unit is 96 metres.

3) Munduran Creek seam. The Munduran Creek seam is divided into three oil shale beds separated by claystones. The basal oil shale bed is the best developed. It consists of dark to moderate yellowish-brown oil shale. Towards the base it is typically carbonaceous. The two upper oil shale beds are less well developed with interbedded greenish-grey to greyish-olive and minor grey claystone. The average thickness of the seam is 35 metres with an estimated 352×10^6 barrels of oil with an average yield of 96 litres per tonne. Like the Teningie Creek, Ramsay Crossing and Brick Kiln seams, the Munduran Creek oil shale beds attenuate on the south-eastern flank with a corresponding increase in claystone, commonly silty to sandy.

4) Humpy Creek. This seam is characteristically carbonaceous. It consists of interbedded brownish-black carbonaceous shale and oil shale, brown oil shale, carbonaceous claystone and rare coaly beds and green claystone. In the northern part of the graben, the top of the seam can be defined by a carbonaceous claystone and the base by a coaly bed. To the south, coaly beds clearly define the boundaries. The seam is generally non-calcareous and pyrite is common in the southern part of the graben. The seam has an average thickness of 15 metres and contains 88×10^6 barrels of oil with an average oil yield of 63 litres per tonne.

5) Brick Kiln. The Brick Kiln seam contains the thickest section (up to 110 metres; average 82 metres) of oil shale. It consists dominantly of oil shale beds separated by a number of thin, claystone beds. The oil shale is dark to moderate yellowish-brown, massive to slabby and increasingly calcareous towards the base. Minor amounts of carbonaceous matter are scattered through the seam and there is a carbonaceous interval which ranges from 10 to 20 metres below the top of the seam and is about 5 metres thick. The seam is sporadically rich in fossils. The seam contains an estimated 1,208 x 10^6 barrels of oil, in-situ, with an average yield of 99 litres per tonne.

6) Ramsay Crossing. This seam consists of two oil shale beds: an upper bed from 5 to 10 metres thick and a lower bed up to 29 metres thick. The main oil shale beds are separated by low-oil-yielding and barren claystone with minor (up to 1.8 metres thick) tough limestone. The lower oil shale bed is separated by a claystone bed. The oil shale is dark yellowish-brown ranging to grey-olive towards the base and is composed in part of sedimentary breccia, with laminae of light grey clays and carbonaceous matter. The oil shale in the upper bed is also yellowish-brown. Claystones (at times carbonaceous) flank the oil shale. Limestone is persistent above the oil shale. The average thickness of the seam is 44 metres and contains 417 x 10^6 barrels of oil with an average yield of 104 litres per tonne.

7) Teningie Creek. A complete section of the Teningie Creek seam was intersected in one drill hole from 272 to 548 metres. The seam consists of three major oil shale sections

(272 to 318 metres, 382 to 454 metres and 488 to 538 metres) where the oil shale is interbedded with low grade oil shale and barren claystones. The oil shale is dark to moderate yellowish-brown with olive gradations. The seam is strongly calcareous at some intervals and there are small discontinuous limestone beds (up to 1 metre thick) and coal bands (less than 0.1 metre thick).

Curlew formation

The uppermost (and youngest) formation of The Narrows bed consists dominantly of greenish-grey to pale grey claystones with interbedded black carbonaceous to coaly shale and minor calcareous sandstone and limestone beds. The base of the formation is well defined by a thick carbonaceous shale and grey claystone bed which grades into carbonaceous oil shale for up to 5 metres above Kerosene Creek seam. Maximum thickness is 119 metres.

Worthington formation

This includes the lowermost sedimentary rocks (oldest) of The Narrows. Its upper contact is defined as the base of the first oil shale bed of the Rundle formation. Its full stratigraphic thickness is unknown.

Dolerite intrusion

The intrusion is encountered at different stratigraphic levels ranging from the Teningie Creek seam to Brick Kiln seam. The upper contact of the intrusion appears to be dome-shaped. The intrusion thermally metamorphosed the invaded sediments causing induration, carbonisation and destruction of kerogen. This intrusion occurs in the central-north part of the Stuart deposit which is 20 km northwest of Gladstone and is contiguous with the Rundle deposit.

D) Organic petrology

The organic matter in the Rundle oil shale deposits consists predominantly of alginite B with minor Botryococcus sourced alginite A and particulate corpohuminite (a huminite submaceral - huminite being the brown coal equivalent of the vitrinite of black coals) (Hutton et al.,1980). Alginite B displays yellow to orange or brown autofluorescence and occurs mostly as thin lamellae less than 0.005 mm thick and 0.05 to 1.5 mm long. A variety of alginite B at Rundle is characterized by its greater thickness, intense green/yellow fluoresence and its occurrence as discrete bodies 0.05 mm to 0.3 mm in length. Typically, such algal entities comprise several lamellae and often incorporate or surround quartz grains, possibly indicating a benthic habitat. This type of alginite comprises less than 1% by volume of the shale.

Maceral analysis of the Rundle oil shale has shown that Fischer Assay yields are proportional to the percentage of algal material present (Hutton et al., 1980). This suggests that a large part of retort yield at Rundle is derived directly from a discrete organic matter with only a small proportion being derived from organic compounds adsorbed onto clay mineral. Spent shales from Fischer analysis contain no fluorescing organic matter or entities referable to alginite. Cutinite and corpohuminite are both recognisable in the residue and show a significant increase in reflectance (Hutton et al., 1980). This is taken to indicate that the bulk of hydrocarbons released upon retorting is derived directly from lamellar alginite and that the alginite is almost wholly converted to gaseous and liquid hydrocarbons.

3. Methods for the chemical analysis of synthetic fuels and oil shale: A Review

A) Preliminary separation techniques

(i) Synthetic fuels

Shale oils are complex mixtures of paraffinic, olefinic and aromatic compounds containing significant quantities of nitrogen and sulphur compounds. Previous workers have reported the presence in shale oils of alkanes, alkenes, pyridines, quinolines, pyrroles, nitriles, thiophenes, phenols, ketones and polyaromatic hydrocarbons. A detailed knowledge of the constituents of crude shale oil is essential for the development of techniques for its subsequent refining and safe handling. Also knowledge of the constituents is needed for the assessment of certain fractions as potential feedstocks for the chemical industry. In order to investigate the constituents, it is necessary to use various techniques to isolate different classes of compounds. The literature available on separation techniques is quite large and therefore it is not possible to cite all the literature in the present review.

(a) Open column chromatography

Liquid chromatography has been carried out on single adsorbents or adsorbent combinations using low boiling alkanes as mobile phase. In this way, saturated hydrocarbons have been separated from other constituents of heavy petroleum fractions. However, recovery has been found insufficient in some cases, for example, long chain alkanes tend to remain on alumina (Evans et al., 1957). Using alumina overlying silica gel, recovery of saturated hydrocarbons has

been demonstrated to be dependent on adsorbent ratio (Gearing et al., 1978). Recovery from silica gel has proved to be excellent for high molecular weight hydrocarbons (Seifert, 1977). Losses of saturated hydrocarbons during chromatographic separation have at least partly been attributed to their interaction with asphaltenes (Nagy et al., 1960; Hamway et al., 1962). However, contradictory results concerning this point do exist (Snyder and Roth, 1964). Dinneen et al. (1955) employed adsorption on Florisil together with vacuum distillation, thermal diffusion and adduct formation for the analysis of hydrocarbons in a high boiling shale oil distillate. Poulson et al. (1972) pointed out that the classical displacement chromatographic method employing silica did not separate classes of compounds cleanly. Smith et al. (1950) used Florisil to separate nitrogen compounds from hydrocarbons in shale oil. Florisil and silica gel adsorption chromatography, followed by mass spectrometry was used to characterize saturates and olefins in a shale oil gas oil fraction (Jensen et al., 1968). Jackson et al. (1974) also used Florisil for a preliminary separation of hydrocarbons from aromatics in a shale oil distillate.

A combination of ion-exchange, co-ordination (using Attapulgus clay treated with ferric chloride) and adsorption chromatography (silica gel) was employed by Jewell et al. (1972), for the separation of petroleum distillates. This method has also been used to separate coal-derived products into five fractions: acids, bases, neutral nitrogen compounds, saturated hydrocarbons and aromatic hydrocarbons. This method

is commonly known as SARA technique (saturates - aromatics - resins - asphaltenes) and is widely used. Co-ordination chromatography has been used to separate nitrogen compounds by complex formation using Attapulgus treated with ferric chloride. Hartung and Jewell (1962a) used this method for identification of nitriles in petroleum products whereas Selucky et al. (1977) in their characterization of Athabasca bitumen used this technique to separate nitrogen compounds.

The analytical group at Oak Ridge National Laboratory has developed a fractionation scheme using acid-base extraction followed by solid-liquid chromatography on Sephadex LH-20, silicic acid and basic alumina (Rubin et al., 1976; Jones et al., 1977). They reported the separation of aliphatic and aromatic hydrocarbons as well as nitrogen heterocyclic and polar aromatic compounds in crude oils derived from coal and shale. Wilson et al. (1981) used a similar solvent fractionation scheme to analyse coal liquefaction products before and after hydrotreatment. They reported the presence of neutral polycyclic aromatic hydrocarbons and sulphur, oxygen and nitrogen heterocyclic aromatic compounds. Schiller and Mathiason (1977) developed a chromatographic procedure using neutral alumina to separate saturated hydrocarbons, aromatic hydrocarbons, benzofurans, ethers, nitrogen compounds and hydroxyl compounds in coal derived liquids.

Later et al. (1981) developed a two-step separation method using neutral alumina to separate aliphatic hydrocarbons, neutral polycyclic aromatics, nitrogen polycyclic aromatics and hydroxyl polycyclic aromatics and silicic acid to separate the nitrogen polycylic aromatics in solvent-refined coal liquids.

Adsorption chromatography on basic and neutral alumina was used to separate nitrogen compounds in hydrotreated shale oil products (Ford et al.,1981). A clean separation of alkanes and alkenes has always been difficult to achieve since they are both non-polar. Silica gel impregnated with silver nitrate has been used to separate alkanes and alkenes in synthetic fuels (Iida et al., 1966; Selucky et al., 1977). Gel permeation chromatography using Sephadex LH-20 has been used for separation of high molecular weight material (Novotny et al., 1974; Jones et al., 1977). The advantage with gel permeation chromatography is that there is little interaction between the gel and compounds.

(b) Liquid - liquid extraction

Uden et al. (1979) characterized the acid and base fractions in shale oil by extracting the oil with aqueous sodium hydroxide and sulphuric acid. This is the classical method for separation of acid and base fractions from neutral compounds. Schultz et al. (1977) and Novotny et al. (1980) used a combination of aqueous sodium hydroxide and sulphuric acid to separate acidic and basic compounds, and extraction with aqueous methanol and nitromethane to separate polar neutrals and polynuclear aromatics respectively from aliphatic neutrals in solvent refined coal products. It has been found that indoles, carbazoles and phenazines react with 72% perchloric acid permitting separation from the aromatic phase. This technique is based on the finding that indole and carbazole nitrogen exhibits basic properties toward perchloric acid and that the resulting perchlorates are soluble in perchloric acid. Hartung and Jewell (1962b) used this technique to isolate carbazoles and phenazines in

petroleum products. Liquid - liquid partitioning using dimethylformamide/water was utilized to separate the aliphatic hydrocarbons from polyaromatic hydrocarbons in a neutral shale oil fraction (Hertz et al., 1980). This method has been reported previously by Bjorseth (1977). Solvent extraction and partitioning of polar types of compounds can cause formation of tars and stable emulsions which contribute to the loss of components and inefficient separations (Clark et al., 1975).

(c) High performance liquid chromatography (HPLC)

With increasing interest in synthetic fuels there is a need for rapid analysis of components and high performance liquid chromatography is widely used for this purpose. The success of this technique depends on the type and size (typically several microns in diameter) of the packing material. Silica gel columns have been shown to rapidly separate hydrocarbon group-types using hexane, heptane and fluorinated solvent mobile phases (Sautoni and Swab, 1975, 1976; Sautoni and Garber, 1976). Limitations to this technique are that polar components are retained on the column packings with such mobile phases and stepping to more polar mobile phases for elution of this class of compounds produces re-equilibration difficulties. An amino-bonded normal phase column packing (NH_2 bonded to silica) has been used to separate hydrocarbon group-types such as saturates, aromatics and polar compounds (which are backflushed off the column) in asphalt, coal liquefaction samples and shale oil (Dark and McGough, 1978; Dark and McFadden, 1978; Wise et al., 1977). However, due to their reactivity with primary amine groups, aldehydes

and ketone solutes should be avoided with an NH_2 bonded phase, thus limiting the use of such columns. Also no separation of saturates and olefins is achieved. Separation of saturates and olefins has been attempted on silica columns using fluorinated mobile phases but with incomplete separation (Sautoni et al., 1975). DiSanzo et al. (1980) used a combination of silica gel (32 - 63 μm Woelm) and silica gel impregnated with silver nitrate to separate alkanes, alkenes and aromatics in shale oil. It should be mentioned that non-chemically modified supports such as silica and alumina are not suitable in HPLC separations requiring high resolution. They can only be used in low-resolution separation of compound groups.

Detailed studies of molecular structure and substituent effects on the retention characteristics of aromatic hydrocarbons on alumina (Snyder, 1966), silica (Popl et al., 1976) and various bonded silicas containing $-C_{18}$, $-NH_2$, $-R(NH_2)_2$, -CN, RCN, pyrrolidone and -DNAP (2,4 - dinitroanilinopropyl) (Wise et al., 1977; Chmielowiec and George, 1980; Mourey et al., 1980; Grizzle and Thompson, 1982; Snyder and Schunk, 1982) have been reported and utilized in the analysis of polyaromatics in shale oil and coal oil.

(ii) Oil shale

Kerogen has been defined as the organic matter in sediments which is insoluble in organic solvents. By far the major portion of organic matter within the biosphere and geosphere combined is in the form of kerogen and this material is now believed to be the source of petroleum

and natural gas. Currently there is much interest in the structure of kerogens since they represent, especially in the case of oil shales, a valuable fossil fuel reserve which has so far been only marginally exploited. A recent review by Yen (1976) emphasizes that the development of fossil fuel technology depends heavily upon an understanding of kerogen structure. The kerogen structure is also interesting from the viewpoint of paleoenvironmental studies of the origin, evolution and distribution of life at the unicellular level. Therefore, techniques must be devised to separate and characterize the kerogen, with minimal alteration of compounds occurring.

(a) Separation of kerogen

Extraction with an organic solvent is a method commonly used to extract the soluble portion of the kerogen. Unfortunately, the soluble portion, "bitumen", represents only a small percentage of the total organic material. It is useful, however, for our understanding of the history and origin of kerogen. In most cases, extraction of the ground rock by ultrasonic agitation at room temperature or Soxhlet extraction at the boiling point of the organic solvent (Robinson, 1969) has been used. Some of the solvents which have been employed are: benzene (Anders et al., 1973); benzene/methanol 1:1 (Seifert, 1978), 2:1 (Wszolek et al., 1972), 3:1 (Simoneit and Burlingame, 1973), 4:1 (Burlingame et al., 1969a), 6:4 (Ishiwatari and Machihara, 1982a), 9:1 (Hodgson et al., 1968); chloroform/acetone/methanol, 47:30:23 (Allan et al., 1980); chloroform/methanol 4:1 (Brown et al., 1980); and methylene chloride (Wakeham et al., 1980b). The amount of extractable material increases with

extraction temperature and with polarity and chemical reactivity of the solvent. Vitorovic and Pfendt (1967) have found that solubilities of Aleksinac oil shale range from 0.53% in petroleum ether to 52.6% in aniline. In the latter case oxidation and chemical alteration occurred. Arpino and Ourisson (1971) have suggested that when methanol or ethanol is used as solvent, esterification of acidic groups may occur, particularly when clay minerals are present to act as catalysts.

Chemical methods have been used to remove inorganic minerals from the kerogen (Saxby, 1970). For many oil shale samples, treatment with hydrochloric acid (to remove carbonates) and with hydrofluoric acid (to remove silica and silicates) are sufficient to give a more or less mineral free kerogen. For the removal of pyrite, lithium aluminium hydride and nitric acid have been used. However, interaction of the dimineralizing agents with organic functional groups in kerogen may occur (Saxby, 1970). Upon HCl and HF treatment, the kerogen nitrogen content decreases, kerogen solubility increases and large losses of organic matter occur.

(b) Characterization of kerogen

Alkaline permanganate as well as other oxidative degradation reagents have been used in the past for the investigation of the chemical structure of different kerogens. Controlled oxidation of kerogen yields small molecules which can be separated and identified and which ideally can be rebuilt into the polymeric kerogen structure. The mode of preparation of the starting material is of particular significance in such studies since unbranched

aliphatic acids, branched acids, dicarboxylic and aromatic acids as well as many other nonacidic products are known to be components of the non-kerogen portion of shale and should be removed before attempting to study the structure of kerogen.

The various oxidants that have been used include, potassium permanganate, chromic acid, hydrogen peroxide and ozone. In the study of the Green River kerogen, alkaline permanganate and chromic acid were most often used (Robinson et al., 1953, 1956, 1961, 1963; Burlingame and Simoneit, 1968; Burlingame et al.,1969a; Djuricic et al., 1971; Vitorovic et al., 1974). Permanganate oxidation is most popular because one can expect oxidative attack primarily at, or next to, a carbon atom bearing a functional group. Two effects are readily observed during alkaline permanganate oxidation:

(1) a good yield of benzene carboxylic acids from highly condensed aromatic structures and

(2) the resistance of fatty materials to attack.

In all types of chemical degradation (hydrolysis and oxidation) at least part of the product may result from loosening of the kerogen matrix and removal of entrapped compounds, which might subsequently react further.

Direct techniques have been used to characterize kerogen. Nuclear magnetic resonance (NMR ^{13}C) using cross polarization and magic angle spinning has been applied to solid samples of oil shales and kerogen concentrates to yield valuable information on the chemical nature of the organic carbon present

(Marciel et al., 1978; Marciel et al., 1979; Resing et al., 1978 and Vitorovic et al., 1978). Other techniques include thermal chromatography (Reed et al., 1974), laser pyrolysis - gas chromatography (Hanson et al., 1975) and differential scanning calorimetry (DSC) (Rajeshwar et al., 1981).

4. Aims of the research

The aims of this thesis are:

(1) Development of a suitable separation scheme to characterize the various organic components in Rundle shale oil.

(2) A comparative analysis of the chemical composition of shale oil extracted by the Fischer Assay retort from various stratigraphic levels in the Rundle deposit.

(3) A study of the chemical composition of shale oil extracted from the Kerosene Creek seam (Rundle deposit) by the Lurgi-Ruhrgas process, in an effort to compare this process with the standard laboratory Fischer Assay retort.

(4) To study the maturation history and origin of the kerogen from the Rundle deposit by examining the solvent extractable components and the kerogen degradation products from the Kerosene Creek oil shale.

(5) To examine the effect of an igneous intrusion on the chemical composition of an oil shale from the Rundle deposit by studying the solvent extractable components and the kerogen degradation products.

EXPERIMENTAL

1. Sample preparation

A) Fischer Assay method

(i) Sampling of oil shales

In 1978 Southern Pacific Petroleum drilled 21 core holes intersecting the various stratigraphic levels of the Rundle deposit. Intersection of the seams is partial where the particular seam subcrops beneath the overburden cover, and in some cases because of faulting (Table 1). Sampling was done at regular 2 metre intervals except for 6 samples (Table 1) which came from 4 metre intervals. The large sample size from each seam indicates that the samples are representative of the Rundle deposit as a whole. The area where the core holes were taken is shown in Figure 4.

(ii) Fischer Assay retorting

All the oil shale samples were sent to A.C.I.R.L. (Australian Coal Industrial Research Laboratories) where each sample was retorted by the Fischer Assay method in 1978. The individual assay samples were stored in stoppered test tubes from the time of assay until early 1980, when they were pooled. The Fischer Assay retorting is a standard laboratory method for extracting oil from oil shales. This method is described by Stanfied and Frost (1949) and is as follows:

The oil shale samples are crushed to -2.4 mm (a minus sign indicates the material that passed the sieve of that size). A 100 g sample is then charged into the cast-aluminium retort in five layers (Figure 5). The layers of

Table 1. Core holes drilled through the Rundle deposit as indicated in Figure 4

Seam	No. of holes intersected		No. of assays represented in sample
	Complete Unit	Partial	
Kerosene Creek	4	6 (3 almost complete)	190
Munduran Creek	5	-	91
Brick Kiln	5	9 (2 almost complete)	358
Ramsay Crossing	12	1	217

No. of assays per seam per core hole. Assays are for 2 metre intervals except for 4 metre intervals indicated in brackets (1). Incomplete intersections are indicated * for upper contact eroded or weathered; # for faulting; + hole not taken deep enough.

Core hole	Kerosene Ck.	Munduran Ck.	Brick Kiln	Ramsay Crossing
65	20			
66	22	19	37	2+
68			33	25
70	23*	16	45(1)	25
76		25	54	17(1)
77	22	22(1)	15#	
78	16(1)			
79			30*	23
80			38*	23
82			24*	12
83	5(1)#			
84			8*	11
85			15*	19
86		11	38(1)	24
88			8*	14
89			8*	12
92	44*			
93			5(1)*	10
94	13#			
96	8*			
97	17#			

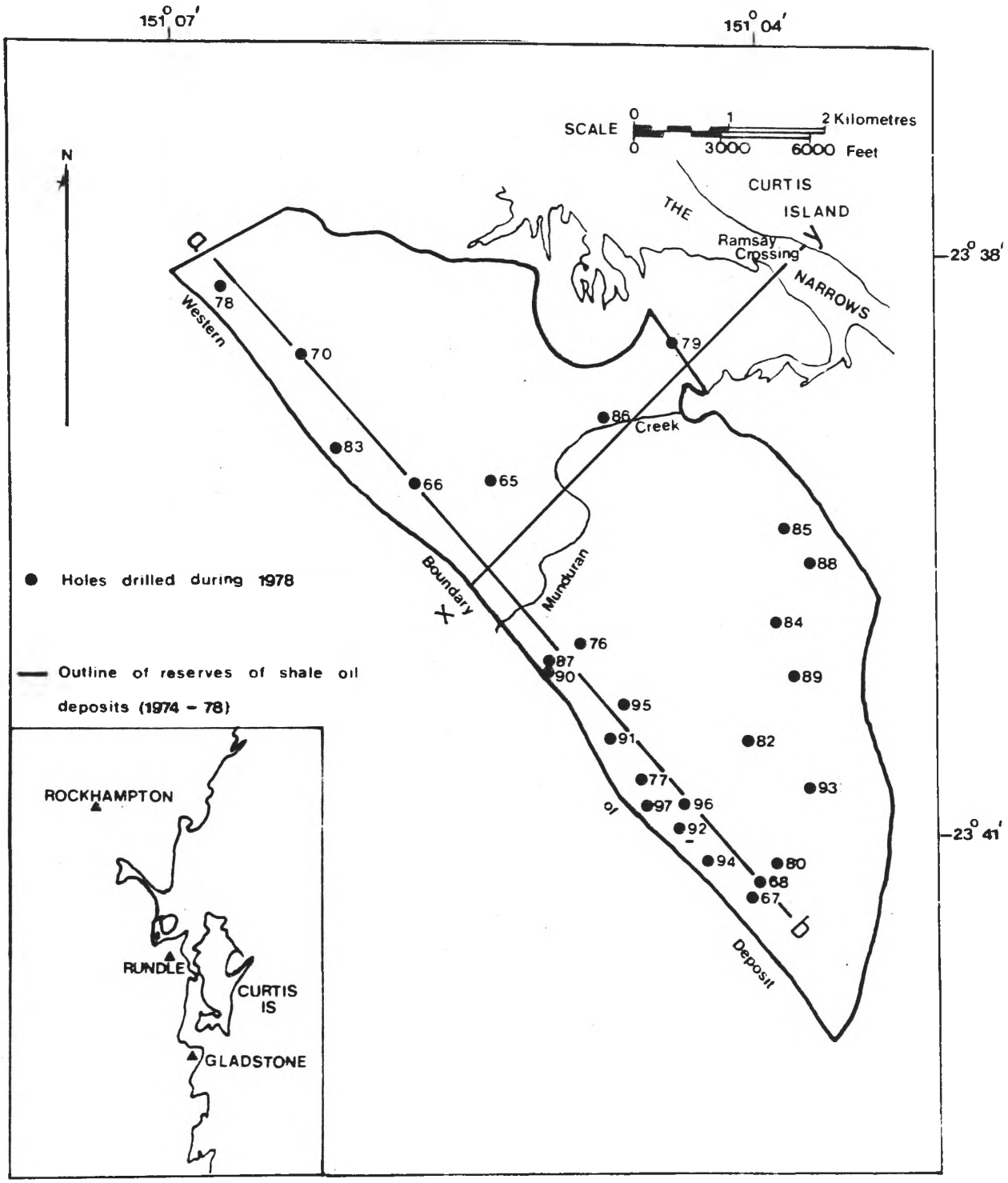
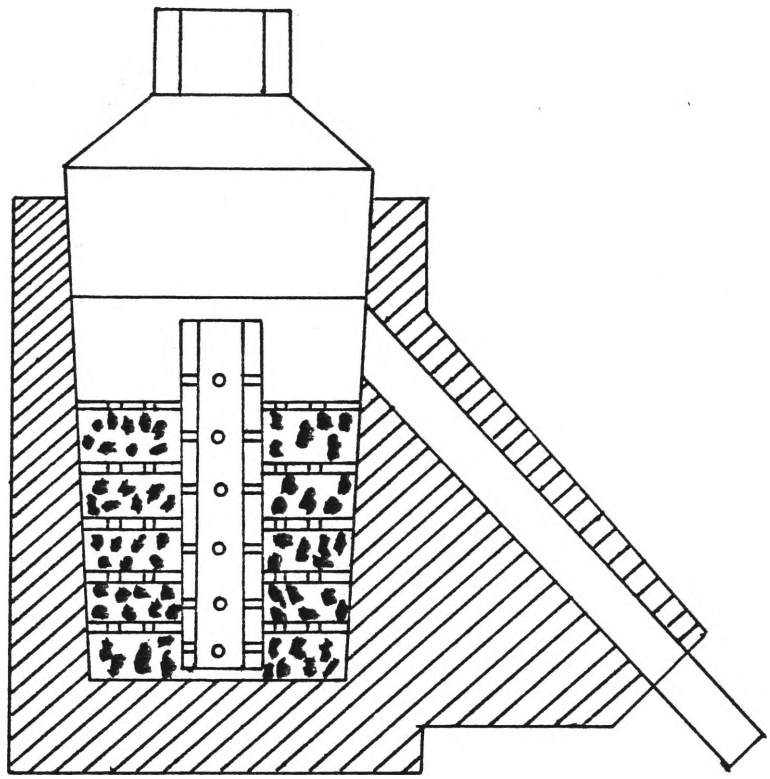


Figure 4. Outline of the Rundle oil shale deposit showing core holes

(A)



(B)

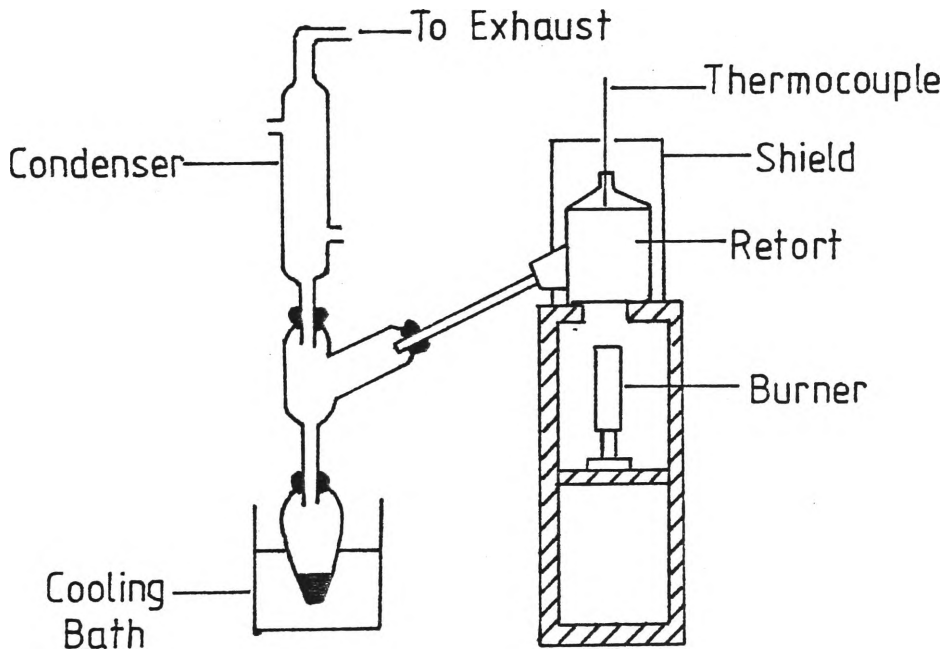


Figure 5. (A) Cast-aluminium retort

(B) Fischer Assay retorting unit

the shale are separated by perforated aluminium disks about a central vent tube. The aluminium disks increase the transmission of heat and render the mass more permeable to oil vapours. The distillate outlet tube from the retort is of stainless steel and connects to a glass adaptor by a teflon plug. The glass adaptor is then connected to a water condenser and a collecting tube immersed in a cooling bath. This arrangement is illustrated in Figure 5. The retort is heated by a gas burner at such a rate that after 40 minutes, a temperature of $500^{o}C \pm 5^{o}C$ is reached. This temperature is maintained until no further oil distils and then the apparatus is cooled. The collecting tube is warmed slightly (approx. $37^{o}C$) to facilitate oil drainage and the distillate is centrifuged to separate the oil and water. Warming facilitates this process.

B) Lurgi-Ruhrgas method

In 1980 Southern Pacific Petroleum retorted oil shale from the Kerosene Creek seam (Rundle) in Herten, West Germany, by the Lurgi-Ruhrgas (L-R) process. The L-R process uses a flash pyrolysis unit which has been in commercial scale operation to carbonise various coals, to crack crude oil, fuel oils and naphtha into olefins and is now being applied to produce synfuels from oil shales and tar sands. The L-R process was developed in the late forties by Lurgi in collaboration with Ruhrgas for the carbonisation of coal fines.

The process is based on a heat transfer to the feed material by solid heat carriers produced in the process. Its heart is the solid heat carrier circulating system named

'loop' (Figure 6) which includes a lift pipe (1) to convey and reheat the circulating fine-grained heat carrier; a collecting bin (2) to separate the combustion gas from the hot heat carrier; a mixer (3) which mixes the hot heat carrier and the raw feed material to induce retorting; a surge bin (4) which provides surge capacity and time to complete retorting. On the product gas side of the loop are a cyclone (5) and a condensation system (6). On the flue gas side of the loop are a cyclone (7) and the flue gas system (8) which includes a waste heat recovery and final electrostatic dedusting. Hot residue is withdrawn from collecting bin (2), cyclone (7) and electrostatic precipitator (8) and is passed through a waste heat recovery unit before being disposed.

In the 'loop', raw oil shale, crushed to approximately 6.5 mm and preheated to approximately 150 - 200°C is fed to the screw mixer where it is mixed with three to four times as much hot spent shale at 650 - 700°C from the collecting bin. The raw shale is thereby flash heated to about 500 - 530°C and retorted within a few seconds. The spent shale leaving the mixer passes to the surge bin where retorting is completed and is then transferred to the lower section of the lift pipe. Combustion air, preheated to about 450°C, is introduced at the bottom of the lift pipe. The air simultaneously conveys the material to the top of the lift pipe while it burns the residual carbon from the spent shale. The combustion gas and reheated spent shale are separated at about 650 - 700°C in the collecting bin. The spent shale is returned to the mixer thereby closing the 'loop'.

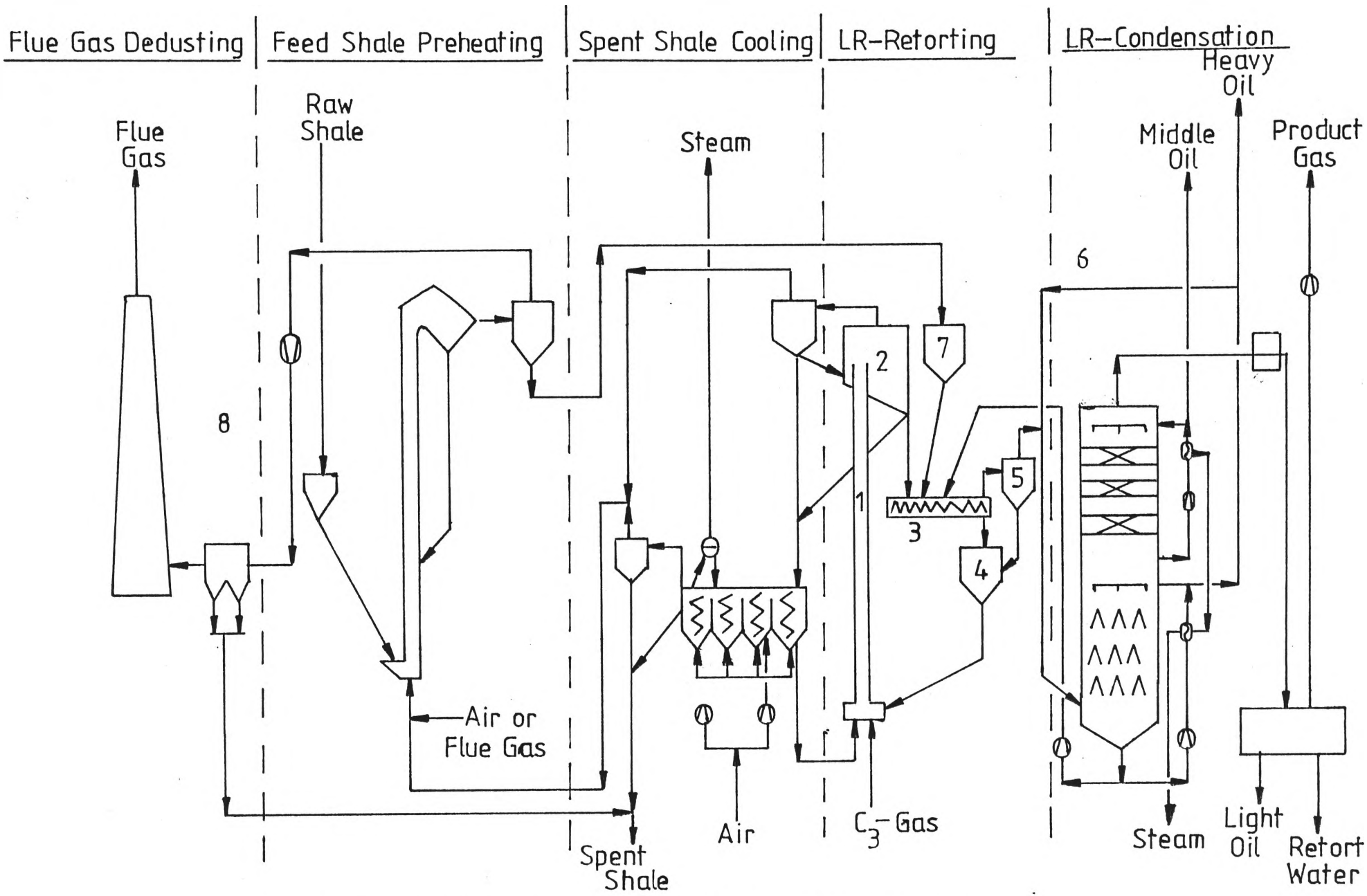


Figure 6. Schematic diagram of the Lurgi-Ruhrgas process

The condensation system shown on the right side of the L-R loop (Figure 6) consists mainly of a catalytic cracker fractionator type condensing tower and a final air cooler condenser. The condensing tower consists of two stages. In the lower stage a heavy oil is condensed and residual dust is removed. In the upper stage of the condensing tower a dust free medium oil is condensed. In the final air cooler - condenser, light oil, naphtha and gas liquor (retort water) are condensed leaving a high BTU retort gas at approximately 50°C which may be used as feedstock for a downstream hydrogen production, or as fuel. In the 1980 test trial the temperatures at which the various oil fractions were collected are as follows:

(a) heavy oil, 220° - 520°C

(b) middle oil, 200° - 480°C

(c) light oil, 70° - 360°C

(d) naphtha, 20° - 150°C

The naphtha was the only fraction which was not available for chemical analysis.

The shale preheater consists of a vertical riser in which the feed shale is pneumatically elevated and preheated by the hot L-R flue gases. Coarser particles separated from the gas upstream of the main feed shale collecting cyclone may be recycled to the riser. Pressure at the bottom to the riser is controlled by a flue gas blower downstream of the feed shale collecting cyclone. The flue gas is then finally dedusted in an electrostatic precipitator before being discharged to the atmosphere.

C) Solvent extraction

(i) Sampling of oil shales

Two oil shale samples were subjected to Soxhlet extraction, alkaline hydrolysis and alkaline potassium permanganate oxidation to study the origin and maturation history of the kerogen. One sample was taken from the Kerosene Creek seam which is regarded as an immature shale (subjected to very little heat during diagenesis). The other shale was taken near an igneous intrusion which meant the material had been thermally altered (carbonised). The carbonised oil shale was found at 137.3 - 137.7 metres below the surface bedded between two siliceous dolerite seams. The stratigraphic level of this carbonised oil shale is shown in Table 2 along with its neighbouring seams. The two oil shale samples were supplied by Southern Pacific Petroleum. The grid reference for the carbonised shale is 7381000N, 302000E.

Table 2. Stratigraphic level of the carbonised oil shale

Depth (m)	Seam
136.0 - 137.1	carbonised oil shale
137.1 - 137.3	siliceous dolerite
137.3 - 137.7	carbonised oil shale
137.7 - 137.8	siliceous dolerite
137.8 - 137.9	carbonised oil shale
137.9 - 141.8	dolerite

2. Chemical separation of shale oil and oil shale

A) Shale oil

(i) Fischer Assay method

The chemical separation of shale oil into various components is similar to the method described by Regtop et al. (1982). Shale oil (5 g) from the various stratigraphic levels in the Rundle deposit was dissolved in hexane (200 ml) and filtered through a 0.45 μm Teflon filter. The insoluble material is classified as asphaltenes. The filtrate was extracted with 3 x 50 ml portions of 10% sodium bicarbonate to isolate the carboxylic acids, 3 x 50 ml portions of aqueous sodium hydroxide (3 M) to isolate the phenolic compounds and then with 3 x 50 ml portions of aqueous sulphuric acid (3 M) to isolate the basic components. The organic phase (neutral fraction) was dried with magnesium sulphate and evaporated to 50 ml on a rotatory evaporator (25°C, 4.7 kPa). The combined sodium bicarbonate extracts and the sodium hydroxide extracts were acidified, extracted with 3 x 50 ml portions of dichloromethane and the organic phases (carboxylic acids and phenolic compounds) were dried with magnesium sulphate and evaporated to the required concentration for g.c. analysis. The combined sulphuric acid extracts were made alkaline and extracted in a similar fashion to yield the basic fraction. The carboxylic acid fraction was evaporated to remove the solvent and methylated with 0.5 ml of 14% BF_3/methanol in a sealed vial for 30 min. at 100°C. The mixture was cooled, diluted with 1 ml of water and the methyl esters were extracted into hexane (2 ml). The hexane insoluble tar (polymeric material) which remained on the glassware after

acidic and basic extraction was dissolved in dichloromethane. The solvent was removed and the tar fraction weighed.

An aliquot (2.5 ml) of the neutral fraction was applied to a combined alumina/silica solumn. The column (120 x 1.5 cm i.d.) was slurry packed, with 22 g of alumina (neutral, activity 1, preheated 12 hours at 300°C) overlying 57 g silica gel (Kieselgel 60, 70 - 230 US mesh, preheated 12 hours at 130°C). The fractions collected, their eluents and contents were as follows: (1) 130 ml hexane, total alkanes; (2) 250 ml hexane, total alkenes and monosubstituted alkylbenzenes; (3) 1 litre hexane, diaromatic hydrocarbons; (4) 250 ml dichloromethane, aliphatic nitriles, 6-alkanones and polyaromatic hydrocarbons; (5) 1 litre chloroform, aliphatic methyl ketones and brown polymeric material; (6) 250 ml methanol, aliphatic amides. All fractions were evaporated on a rotatory evaporator (25°C, 4.7 kPa) to a suitable concentration for g.c. analysis.

The dichloromethane fraction, containing nitriles and polyaromatic hydrocarbons, was evaporated to approximately 1 ml and rechromatographed on an alumina column (30 cm x 1.5 cm i.d.), slurry packed with hexane. The fractions collected, their eluents and contents are as follows: (1) 100 ml 10% dichloromethane in hexane, traces of diaromatic hydrocarbons (if any); (2) 100 ml 50% dichloromethane in hexane, polyaromatic hydrocarbons; (3) 100 ml dichloromethane, aliphatic nitriles and 6-alkanones.

Aliquots of the total alkane and total alkene fractions were evaporated to remove the solvent, dissolved in cyclohexane (3 ml) and refluxed for 6 hours with 0.5 nm molecular sieve

(1.5 g; dried for 12 hours at 300°C). Linear alkanes and alkenes adsorbed to the molecular sieve and were removed by filtration; the filtrates contained the branched/cyclic alkane and branched/cyclic alkene/monoaromatic hydrocarbon fractions.

(ii) Lurgi - Ruhrgas method

The light, middle and heavy oil from the Lurgi process were separated into asphaltenes, acidic and basic fractions using the same procedure as for the Fischer Assay oils.

An aliquot (1 ml) of the neutral fraction from each oil was applied to a combined alumina/silica column using the same column as for the Fischer Assay oils. The fractions collected, their eluents and contents were as follows: (1) 130 ml hexane, total alkanes; (2) 250 ml hexane, total alkenes and monosubstituted alkylbenzenes; (3) 1 litre hexane, diaromatic hydrocarbons; (4) 130 ml dichloromethane, polyaromatic hydrocarbons; (5) 200 ml dichloromethane, aliphatic nitriles, 3-, 4-, 6-alkanones; (6) 500 ml chloroform, methyl ketones; (7) 300-400 ml chloroform, or until brown polymeric fraction elutes; (8) 300 ml, methanol, methyl esters.

The branched/cyclic alkanes and alkenes were separated using the same procedure as for the Fischer Assay oils.

B) Oil shale

(i) Soxhlet extractable compounds

(a) Kerosene Creek oil shale

Oil shale (50 g; crushed to 0.25 mm) was Soxhlet extracted for 72 hours with benzene/methanol (4:1 v/v). The solvent was removed with a rotatory evaporator (25°C; 4.7 kPa) and the residue treated with hexane (50 ml). The hexane insoluble material was collected on a 0.45 μm Teflon filter. The filtrate was extracted with 3 x 20 ml portions of 10% $NaHCO_3$ to isolate carboxylic acids. The organic phase (neutral fraction) was dried with $MgSO_4$ and evaporated to approximately 1 ml on a rotatory evaporator (25°C; 4.7 kPa). The $NaHCO_3$ solution was acidified and extracted with 3 x 20 ml portions of dichloromethane. The organic phase was dried with $MgSO_4$ and the solvent removed on a rotatory evaporator (25°C; 4.7 kPa). The residue (organic acids) and the hexane insoluble material were combined and methylated with 0.5 ml 14% BF_3/methanol in a sealed vial for 30 min. at 100°C. The mixture was diluted with water and the methyl esters were extracted into hexane (2 ml).

The neutral fraction was chromatographed on a column as described previously. The fractions collected, their eluents and contents were as follows: (1) 400 ml hexane, total alkanes and alkenes; (2) 1 litre hexane, mono- and diaromatic hydrocarbons; (3) 300 ml dichloromethane, polyaromatic hydrocarbons (PAH); (4) 700 ml chloroform, porphyrins, aliphatic and steroidal alcohols; (5) 50 ml chloroform, brown polymeric material; (6) 250 ml methanol, amides. The PAH fraction contained traces of long chain alkanes (greater than C_{27}). As a result, this fraction was again chromatographed

on an alumina column (30 cm x 1.5 cm i.d.). Alkanes were eluted with 100 ml hexane and PAH with 100 ml dichloromethane. The alkane fraction was combined with the first fraction. The branched/cyclic alkanes were separated by 0.5 nm molecular sieve as described previously.

An aliquot of the aliphatic, steroid and triterpenoid alcohol fraction was silylated by adding 100 µl of bis(trimethylsilyl)trifluoroacetamide (BSTFA) to the evaporated fraction and the mixture heated in a sealed vial for 30 min. at 100°C.

(b) Carbonised oil shale

This shale was Soxhlet extracted and the acids separated as described above (Kerosene Creek shale). The neutral fraction was chromatographed on an alumina/silica column as described previously. The fractions collected, their eluents and contents were as follows: (1) 200 ml hexane, total alkanes and elemental sulphur; (2) 1 litre hexane, mono- and diaromatic hydrocarbons; (3) 300 ml dichloromethane, polyaromatic hydrocarbons; (4) 500 ml chloroform, porphyrins, aliphatic ketones; (5) 50 ml chloroform, brown polymeric material; (6) 250 ml methanol, amides.

The branched/cyclic alkanes were separated by 0.5 nm molecular sieve as described previously.

(ii) Alkaline hydrolysis

(a) Kerosene Creek oil shale

After Soxhlet extraction, the shale was refluxed for 16 hours with 150 ml of 10% KOH in methanol. The solution was cooled, filtered through a sintered glass crucible and acidified to approximately pH 1. A copious precipitate formed, the bulk of which dissolved upon further dilution with water. The remaining insoluble material (humic acids) was

separated by filtration, washed with ether (3 x 20 ml) and weighed. The ether washings were shaken with the filtrate; the ether extract was dried with $MgSO_4$ and the solvent removed on a rotatory evaporator (25°C; 4.7 kPa). The acids were then methylated as described previously, for g.c. analysis.

(b) Carbonised oil shale

This shale was treated with alkaline methanol using the same procedure as the Kerosene Creek oil shale, except that, since no humic acids formed after acidification, the acidified solution was directly extracted with ether and the extract treated as before.

(iii) Alkaline potassium permanganate oxidation

(a) Kerosene Creek oil shale

After solvent extraction and alkaline hydrolysis, the shale (10 g) was oxidized in a step-wise treatment (7 steps) with small amounts of $KMnO_4$ (1.25 g per step) in 100 ml of 1.6% KOH at 80°C. After the reduction of each portion of reagent the remaining shale was filtered off, suspended in KOH solution as before and treated with the next aliquot of $KMnO_4$. The filtrate from each step was acidified to pH 1. The precipitated (humic) acids were filtered off, washed with ether (3 x 20 ml) and weighed. The ether washings were shaken with the filtrate. The organic phases were dried with $MgSO_4$ and the solvent removed on a rotatory evaporator (25°C; 4.7 kPa). The acids from each step were methylated with BF_3/methanol as described previously.

(b) Carbonised oil shale

This oil shale was oxidized using the same procedure as for the Kerosene Creek seam except that the oxidation was completed after 2 steps. Also, since no precipitated humic acids formed after acidification, the acidified solution was directly extracted with ether and treated as before. In step 2 the $KMnO_4$ was not completely reduced, therefore the solution was treated with $NaHSO_3$ after acidification to reduce excess $KMnO_4$.

3. Instrumental analysis

All fractions were evaporated (rotary evaporator, 25°C, 4.7 kPa; then dry nitrogen jet, 25°C) to a suitable concentration for g.c. analysis or completely for gravimetric quantitation. G.c. analyses were carried out on a Varian Model 3700 gas chromatograph equipped with a flame ionisation detector. Separations were performed on 20 m narrow and wide bore glass capillary columns and on a 25 m vitreous silica capillary column, all wall-coated with SE-54 and programmed from 50 to 280°C at 4°C $min.^{-1}$ (isothermal at 280°C). A 20 m Carbowax 20 M vitreous silica wall-coated capillary column was used for basic nitrogen compounds. The inlet splitter and the pressure drop across the column, in the case of the glass capillary columns, was at 20 : 1 and 55 kPa respectively, whereas in the case of the vitreous silica capillary column the inlet splitter was at 10 : 1 and the pressure drop of 152 kPa. Most of the gas chromatography - mass spectrometry (g.c./m.s.) analyses were carried out on a DuPont Model 21-491B double focussing magnetic sector mass

spectrometer interfaced directly to a Varian Model 2700 gas chromatograph (50 m glass capillary column support-coated with SE-30 and programmed similarly). Towards the end of the research some of the gas chromatography-mass spectrometry analyses were carried out on a Mat 44 quadrupole interfaced to a Varian Model 3700 with a 50 m vitreous silica capillary column wall-coated with SE-30. The mass spectrometric data from the DuPont were acquired and processed, initially, using a Data General Nova Model 1220 data system and then a Data General Nova 4 data system. Direct-insertion mass spectrometry (DI - MS) was also carried out on the DuPont instrument. Porphyrins were analysed by DI - MS using chemical ionization impact with isobutane as reagent gas. The direct insertion probe was programmed from ambient temperature to 300^{o}C and spectra recorded in the range 200 - 250^{o}C. The electron energy was 70 eV and the ion source at 240^{o}C. Proton n.m.r. analyses were carried out on a Perkin-Elmer High Resolution NMR Model R-24 (60 MHz). Compounds were identified by comparison with reference mass spectra (Stenhagen et al., 1974, or otherwise stated) and by the use of mass fragmentography. Isomeric compounds were also identified by coinjection of standards on the gas chromatograph.

RESULTS AND DISCUSSION

1. Fischer Assay retort oil

The analytical procedure used for the separation of the neutral shale oil components (Regtop et al., 1982) was effective only when a mixed bed of alumina and silica was used. Alumina has a high affinity for aromatic and polar compounds and silica separates the alkanes and alkenes. One valuable feature of the method is the facile separation of nitriles and methyl ketones, which otherwise tend to co-elute (Iida et al., 1966).

The oils from all the seams are highly aliphatic in character (H/C = 1.7; Table 3). Alkanes (approx. 30% of the oil and alkenes (approx. 20%) are the most abundant components of the oil (Table 4). A large proportion of the aromatic fraction was found, by proton magnetic resonance, to be in the acidic and basic fractions but these together constitute less than 5% of the oil (Regtop et al., 1982). The aromatic proton resonances in these fractions are due to the presence of phenols and heterocyclic nitrogen compounds respectively. The asphaltenes gave no detectable aromatic proton signal.

The identification of compounds was limited by the fact that the mass spectrometer was a magnetic instrument and hence the fastest scanning rate was 4 - 5 sec. per scan (scan = 40 - 800 amu). Therefore this limited the use of the g.c. column connected to the mass spectrometer to a support-coated glass capillary column because the residence time of the compounds on this type of column is compatible

Table 3. Elemental composition of the Fischer Assay oils

Shale oil	% element in oil[a]					H/C
	C	H	N	S	O	
Kerosene Creek	82.8	11.6	1.3	0.3	2.5	1.7
Munduran Creek	84.3	11.9	1.3	0.4	1.8	1.7
Humpy Creek	85.1	11.7	1.6	0.4	1.9	1.6
Brick Kiln	83.2	11.5	1.3	0.4	1.6	1.7
Ramsay Crossing	84.5	11.9	1.4	0.4	1.5	1.7

a Analyses were performed by the Australian Mineral Development Laboratories, Microanalytical Service

Table 4. Gravimetric results for the Fischer Assay oil fractions

Fraction[a]	Percentage mass				
	Kerosene Creek	Munduran Creek	Humpy Creek	Brick Kiln	Ramsay Crossing
Asphaltene	3.9	2.1	3.4	3.8	1.8
Acidic	1.6	2.5	3.2	1.6	1.7
Basic	2.3	2.5	3.4	2.6	3.1
Tar	11.4	6.5	9.9	6.5	8.9
Linear alkane[b]	22.8	23.9	17.8	24.5	21.2
Branched/cyclic alkane	8.6	11.7	6.6	9.5	5.7
Linear alkene [b]	9.2	11.7	12.7	11.7	15.0
Branched/cyclic alkene and alkylbenzene	8.6	7.1	7.1	6.5	6.9
Diaromatic	6.3	7.2	8.4	6.7	7.4
Polyaromatic	5.0	4.7	5.1	4.2	5.0
Aliphatic nitrile	6.5	11.6	12.5	13.5	11.9
Methyl ketone and polymeric material	9.0	10.1	7.8	8.0	8.0
Amide	5.4	4.3	4.5	4.6	3.1

a Fractions are named according to the most conspicuous compounds present

b These fractions are determined by difference between total and branched/cyclic material using molecular sieve

with the scanning rate of the mass spectrometer. The existing set up on the gas chromatograph (g.c.) could not accommodate a wall-coated glass capillary column (WCOT) and the residence time of the compounds on this type of column is about 2 seconds which is too brief for the existing mass spectrometer. The wall-coated capillary columns have better resolution than the support-coated capillary columns. Therefore a quadrupole mass spectrometer is needed because fast scan rates can be achieved (typically 1 scan per 0.5 seconds). A quadrupole mass spectrometer coupled with a gas chromatograph containing a wall-coated capillary column would facilitate the identification of many more compounds.

A) Alkanes

The straight-chain alkanes in the Kerosene Creek shale oil constitute approximately 20% of the oil (Table 4) and range from C_8 to C_{32} with maxima at C_{10} and C_{27} (Figure 7). This is a typical distribution pattern for the shale oil from the Rundle deposit. The straight-chain alkane distribution from the other seams was similarly bimodal, but the secondary maximum at C_{27} was more pronounced leading to a greater abundance of C_{31} - C_{36} alkanes (Figure A; Appendix). The maximum at C_{10} is uncertain due to losses arising from volatility during sample work up. Alkanes in the region C_{24} - C_{37} probably arise from the pyrolytic fission of kerogen moieties derived from higher plant waxes, because the latter are known to contain linear alkyl chains of suitable length (Eglinton and Hamilton, 1963; Simoneit, 1978). The greater abundance of C_{24} - C_{36} alkanes in the oils from the seams

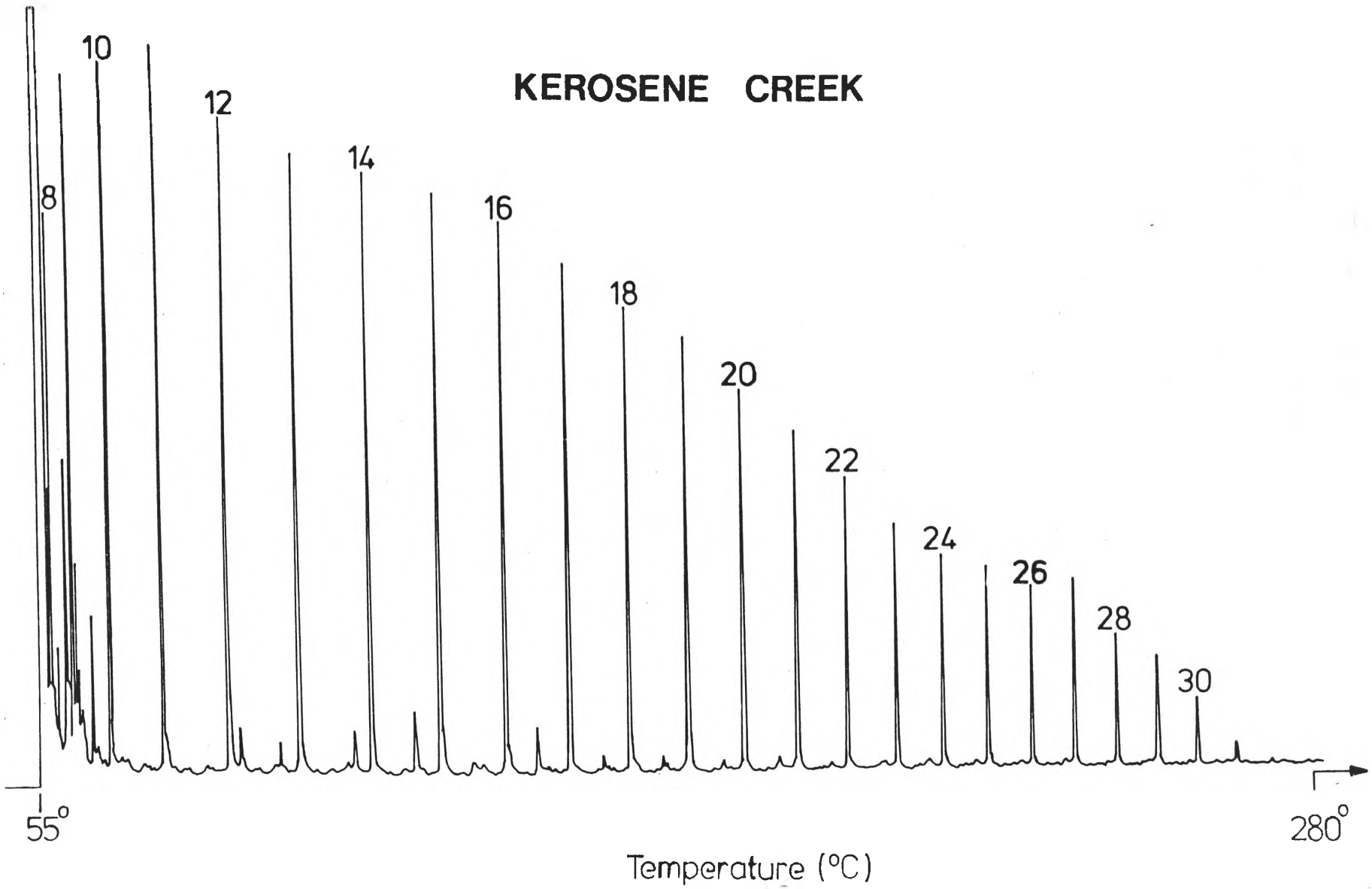


Figure 7. Gas chromatogram of the total alkane fraction from the Kerosene Creek shale oil. Carbon numbers of homologous linear alkanes are indicated.

below Kerosene Creek seam indicates a greater input of terrestrial materials. Alkanes in the range C_8 - C_{23} may be derived from the pyrolytic scission of terrestrial lipid materials or of kerogen moieties derived from algal or bacterial lipids (Oro et al., 1967; Han and Calvin, 1969; Ingram et al., 1983; Regtop et al., 1983). The absence of carbon number preference is likely to arise from a random pyrolytic process.

Branched alkanes constitute less than 10% of the total oil from each shale (Table 4) and comprise homologous series of 2- and 3-methylalkanes, isoprenoid alkanes, alkylcyclopentanes and alkylcyclohexanes (Table 5). The gas chromatogram of the branched/cyclic alkane fraction from the Kerosene Creek shale oil (Figure 8) is a typical profile of the Rundle deposit. The shale oil from the other seams have similar g.c. profiles (Figure B; Appendix). The isoprenoid alkanes ranging from C_{13} - C_{16} and C_{18} - C_{20}, are the most abundant compounds in the branched/cyclic alkane fractions, with the C_{16} being the dominant compound. The absence of the C_{17} isoprenoid is due to the improbability of cleaving two carbon-carbon bonds in an isoprenoid chain (McCarthy and Calvin, 1967). The most likely source of isoprenoid alkanes is the phytol side chain of chlorophyll (Ikan et al., 1975a; Didyk et al., 1978) although carotenoids may be an additional source (Gallegos, 1976). The ratio of pristane/phytane is approximately 2.5 in all the oils.

The ratio of pristane/phytane has been used as an indicator for palaeoenvironmental conditions of sedimentation for crude oils and sediments. Anoxic conditions preserve the C_{20}

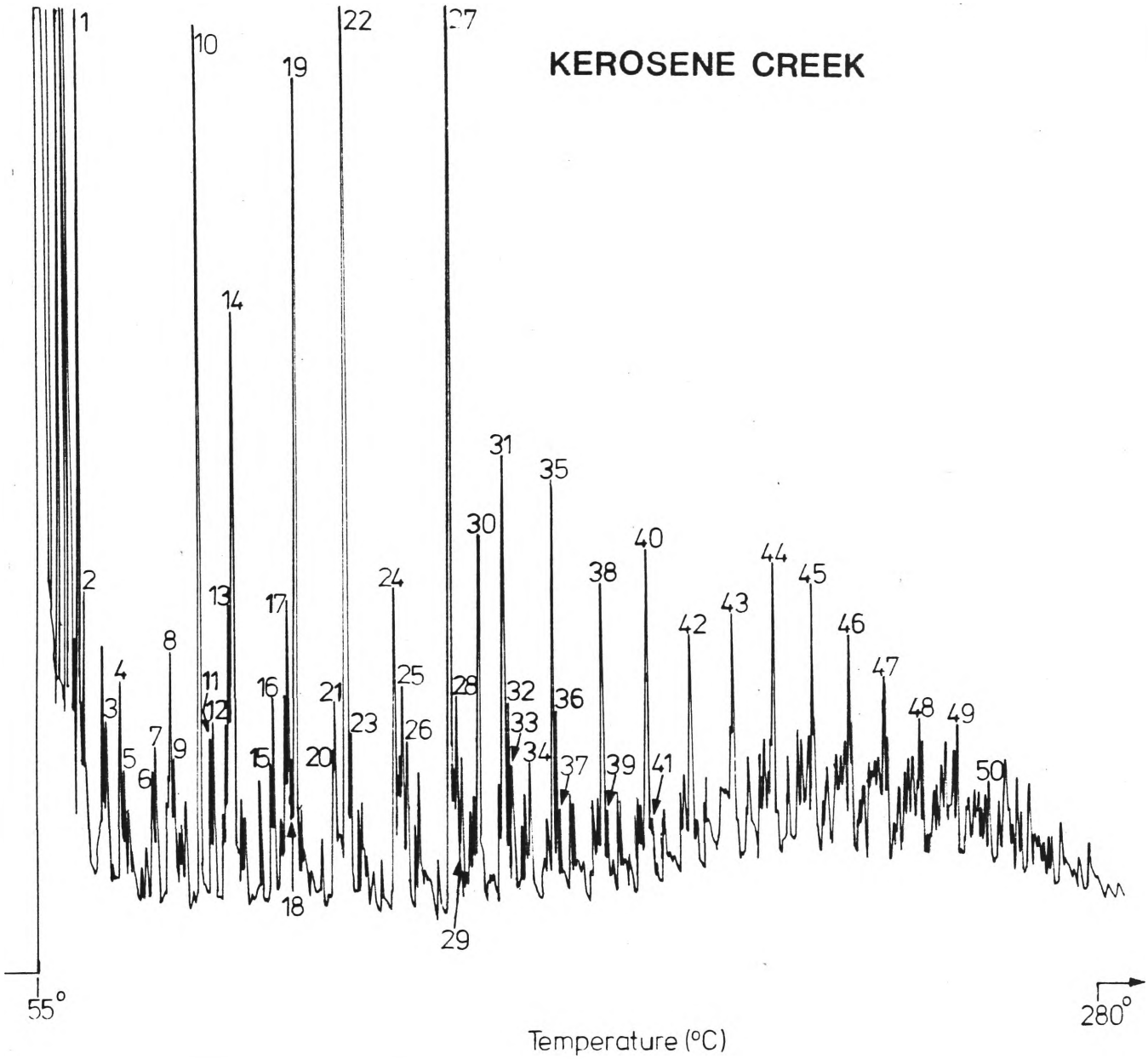


Figure 8. Gas chromatogram of the branched/cyclic alkane fraction from the Kerosene Creek shale oil. Numbers refer to compounds listed in Table 5.

Table 5. Branched/cyclic alkane fraction in the Fischer Assay and Lurgi oils

Peak[1] No.	Identity	Peak[1] No.	Identity
1	2-methylnonane	34	phytane
2	3-methylnonane	35	n-C_{12} cyclohexane n-C_{13} cyclopentane
3	n-C_4 cyclohexane		
4	2-methyldecane	36	2-methyloctadecane
5	3-methyldecane	37	3-methyloctadecane
6	n-C_5 cyclohexane	38	n-C_{13} cyclohexane n-C_{14} cyclopentane 2-methylnonadecane
7	n-C_6 cyclopentane		
8	2-methylundecane	39	3-methylnonadecane
9	3-methylundecane	40	n-C_{14} cyclohexane n-C_{15} cyclopentane 2-methyleicosane
10	2,6-dimethylundecane		
11	n-C_6 cyclohexane	41	3-methyleicosane
12	n-C_7 cyclopentane	42	n-C_{15} cyclohexane n-C_{16} cyclopentane 2-and 3-methylhen-eicosane
13	2-methyldodecane		
14	2,6-dimethyldodecane		
15	n-C_7 cyclohexane	43	n-C_{16} cyclohexane n-C_{17} cyclopentane 2- and 3-methyldocosane
16	n-C_8 cyclopentane		
17	2-methyltridecane		
18	3-methyltridecane		
19	2,6,10-trimethyl-dodecane	44	n-C_{17} cyclohexane n-C_{18} cyclopentane 2-and 3-methyltricosane
20	n-C_8 cyclohexane		
21	n-C_9 cyclopentane		
22	2,6,10-trimethyl-tridecane 2- methyltetradecane	45	n-C_{18} cyclohexane n-C_{19} cyclopentane 2-and 3-methyltetracosane
23	3-methyltetradecane		
24	n-C_9 cyclohexane n-C_{10} cyclopentane	46	n-C_{18} cyclohexane n-C_{19} cyclopentane 2-and 3-methylpentacosane
25	2-methylpentadecane		
26	3-methylpentadecane		
27	2,6,10-trimethyl-pentadecane n-C_{10} cyclohexane n-C_{11} cyclopentane	47	n-C_{19} cyclohexane n-C_{20} cyclopentane 2-and 3-methylhexacosane
28	2-methylhexadecane		
29	3-methylhexadecane	48	n-C_{20} cyclohexane n-C_{21} cyclopentane 2-and 3-methylheptacosane
30	pristane		
31	n-C_{11} cyclohexane n-C_{12} cyclopentane		
32	2-methylheptadecane		
33	3-methylheptadecane		

Table 5. continued

Peak No.[1]	Identity
49	$\underline{n}$-C_{21} cyclohexane $\underline{n}$-C_{22} cyclopentane 2-and 3-methyloctacosane
50	$\underline{n}$-C_{22} cyclohexane $\underline{n}$-C_{23} cyclopentane 2-and 3-methylnonacosane
a	17βH-trisnorhopane ($C_{27}H_{46}$)
b	17αH, 21βH-norhopane ($C_{29}H_{50}$)
c	17βH, 21αH-30-normoretane ($C_{29}H_{50}$)
d	17αH, 21βH-hopane ($C_{30}H_{52}$)

(1) Numbers refer to peaks in Figures 8, 21 and B (Appendix). Letters refer to peaks in Figure 21.

isoprenoid skeleton, giving low pristane/phytane ratios, while oxic conditions cause greater degradation so that the C_{20} skeleton is less likely to survive intact in sediments, leading to a high pristane/phytane ratio (Didyk et al., 1978). Pristane is formed from phytol by an oxidative pathway, for example via phytanic and/or phytenic acids, while phytane is generated through various reductive paths (Figure 9). The pristane/phytane ratio in the shale oil from the Kerosene Creek seam is 2.5 which is higher that the ratio in the corresponding bitumen, which is 1.5 (Regtop et al., 1983). This increase in pristane in the shale oil could be produced by pyrolytic C-C bond cracking of isoprenoid units attached to kerogen (Burlingame et al., 1969a; Tissot and Welte, 1978a). The greater abundance of isoprenoid alkanes with less than the C_{19} skeleton in the shale oils is probably due to further cracking of pristane and phytane during pyrolysis. 2-Methyl-alkanes occur in plant waxes, bacterial waxes and marine organisms (Tissot and Welte, 1978b) and are probably of biological rather than pyrolytic origin. Alkylcyclopentanes and alkylcyclohexanes may arise from the intramolecular cyclisation of unsaturated fatty acids during diagenesis (Philp, 1980). n-Alkylcyclohexanes have been found in petroleum (Philp and Gilbert, 1980).

B) Alkenes

Linear alkenes constitute 10 - 15% of each shale oil (Table 4), with the 1-alkenes predominating, and range from C_9 to C_{34}. The g.c. profile of the Kerosene Creek shale oil is typical of the Rundle deposit (Figure 10). The order of elution of the isomeric alkenes on the capillary columns is

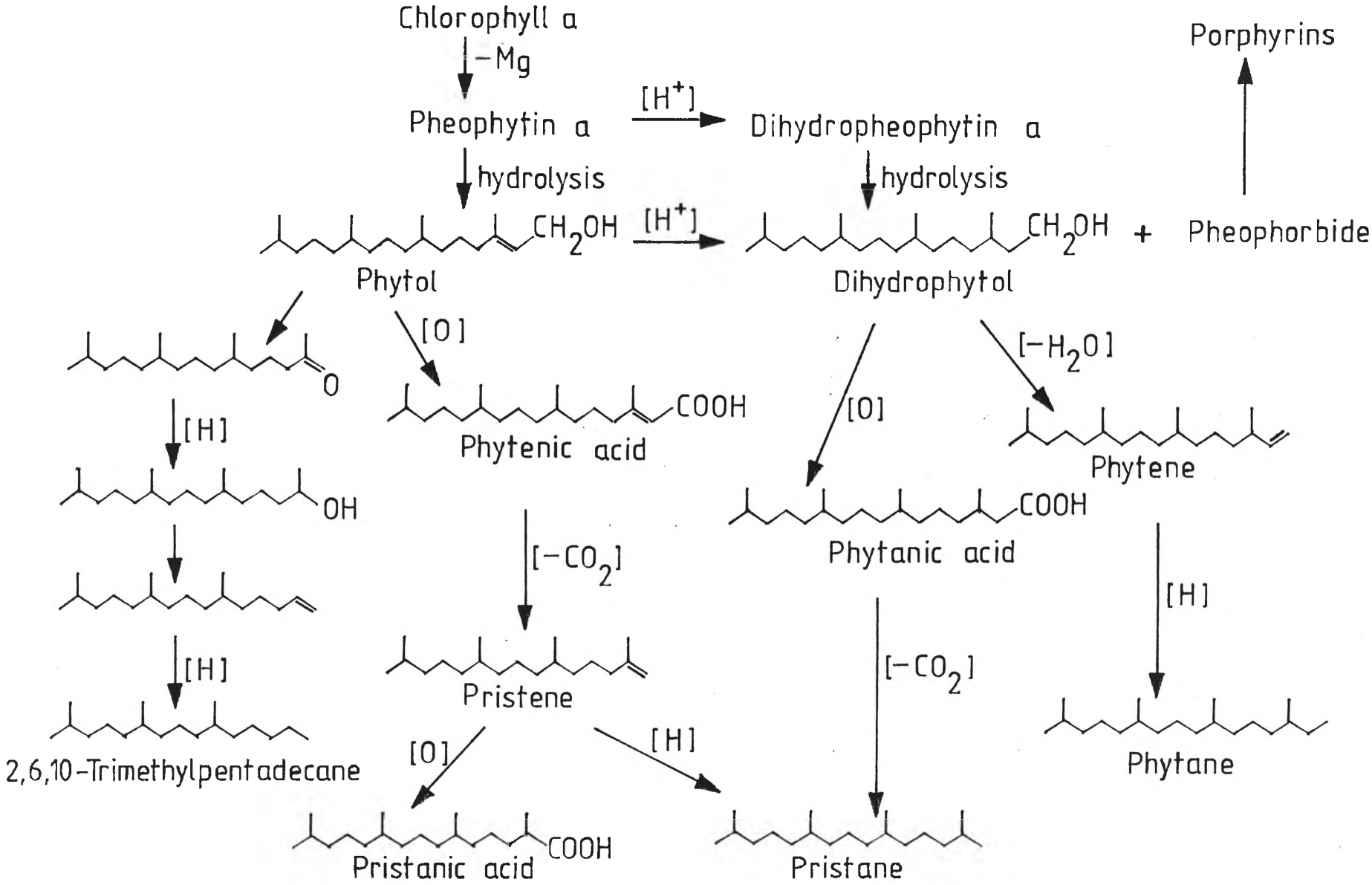


Figure 9. Proposed pathway for the diagenesis of chlorophyll (Didyk et al., 1981)

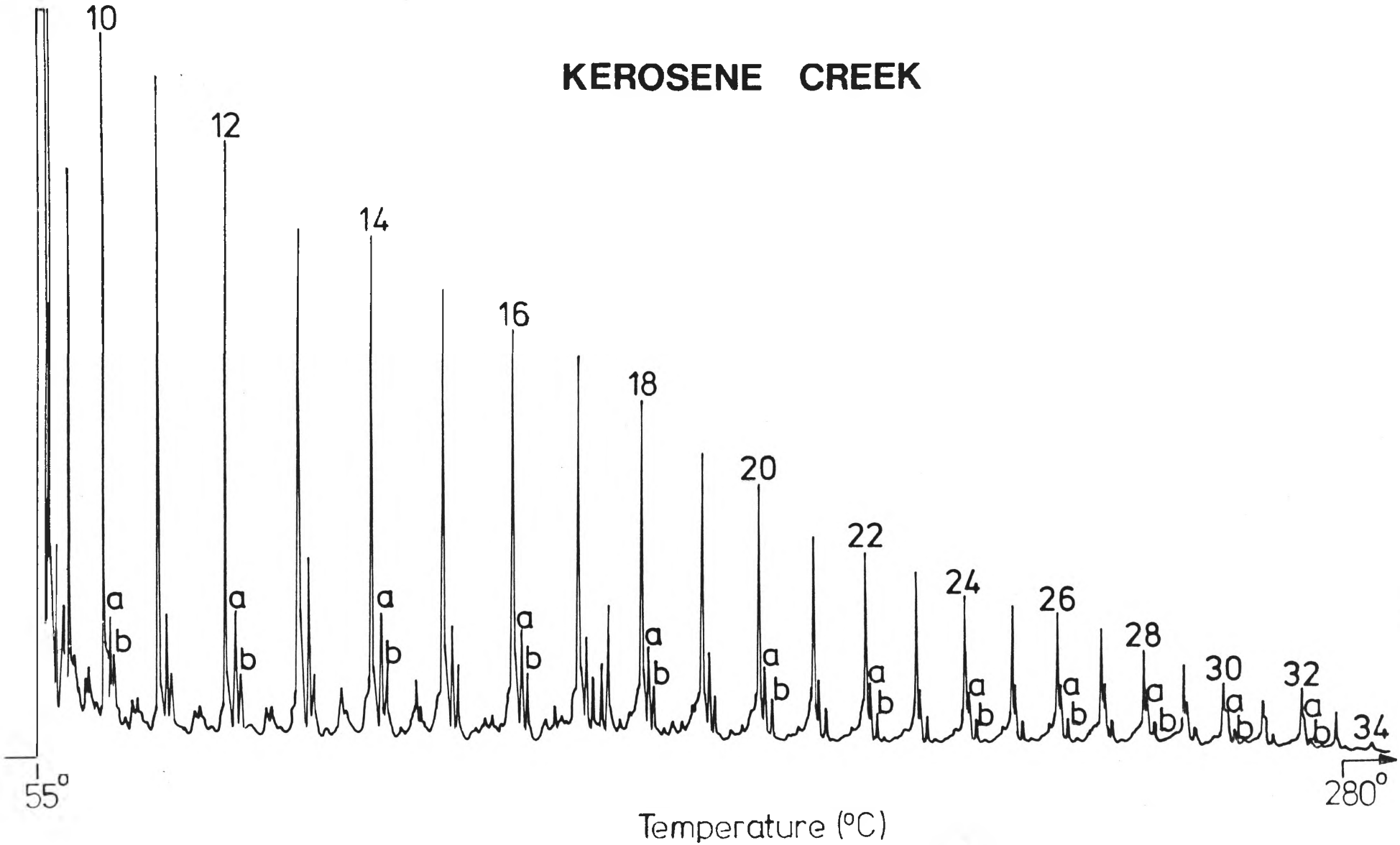


Figure 10. Gas chromatogram of the total alkene fraction from the Kerosene Creek shale oil. Carbon numbers of homologous 1-alkenes are indicated. a and b denote homologous 3- and 2-alkenes respectively.

1-, 4-, 3-, 2-. The 4-alkene was not separated adequately on the glass capillary column that was used and therefore was not detected. Rovere et al. (1983) detected 4-alkenes in the shale oil from the Condor deposit, Queensland, which is a similar deposit to Rundle, using vitreous silica capillary columns and therefore it is most likely that 4-alkenes do occur in the Rundle shale oil. The 1-alkene is the dominant positional isomer at low molecular weights, but its proportion declines markedly with increasing molecular weight. The 1-alkenes have a maximum at C_{10} and a slight plateau at C_{26}. The maximum at C_{10} is not strictly correct due to volatility losses of lower molecular weight alkenes during sample preparation and/or preferential loss of low molecular weight components due to the inlet splitter. The 3-alkenes have a bimodal distribution pattern with maxima at C_{13} and C_{25} - C_{27} for Kerosene Creek and Ramsay Crossing; at C_{13} and C_{25} for Humpy Creek and Brick Kiln and at C_{13} and C_{27} for Munduran Creek (Figure C; appendix). It appears that the 2-alkenes have a slight maximum at C_{14} for all the oils and also at C_{28} in the Munduran Creek oil.

The 1-alkenes may arise from β-elimination reactions of esters or N-substituted amides (DePuy and King, 1960) or from the disproportionation of secondary alkyl radicals (Sykes, 1967). The 2-, 3- and 4-alkenes are thermodynamically more stable than the 1-alkenes (Weast, 1980) and may arise by the thermally induced migration of the terminal double bond in the presence of an acid catalyst (Solomons, 1976). The siliceous nature of the Rundle shale could act as an acidic catalyst during retorting. The Green River shale oil does

not contain isomeric alkenes probably due to the small amount of silica in the largely carbonate matrix (Ingram et al., 1983).

The gas chromatogram of the branched/cyclic alkenes from the Kerosene Creek shale oil (Figure 11) is typical of the Rundle deposit. This fraction also contains an homologous series of alkylbenzenes. The pristene isomers were the most abundant branched alkenes in all the oils (Figure D; Appendix). Other alkenes identified include homologous series of alkylcyclopentenes, 1-alkylcyclohexenes, 2-methyl-3-alkenes and probably 1-methyl-4-alkylcyclohexenes (Table 6). Isoprenoid precursors are indicated for part of the carbon skeleton of the latter two series. The three pristene isomers may be derived from phytol residues in the kerogen by similar processes to those for the linear alkenes or from pristene synthesised by marine organisms (Blumer et al., 1971) and incorporated into the kerogen. For the two series of alkylcycloalkenes there are corresponding series of alkylcycloalkanes suggesting a common origin for these two classes of compounds.

(C) Aromatics

A prominent series of 1- and 2-phenylalkanes (C_5 - C_{27} alkyl chain) was found in the branched/cyclic alkene fraction (Figure 11, D). Rovere et al. (1983) have separated these aromatics from the branched/cyclic alkenes. Polysubstituted benzenes and substituted naphthalenes were found in the diaromatic fraction which constitutes 6 - 8% of the total oils (Table 4). Figure 12 is a typical gas chromatogram of the diaromatic fraction from shale oil of the Rundle deposit. This fraction contains polymethyl substituted benzenes, indans, indenes and homologous series of 1- and

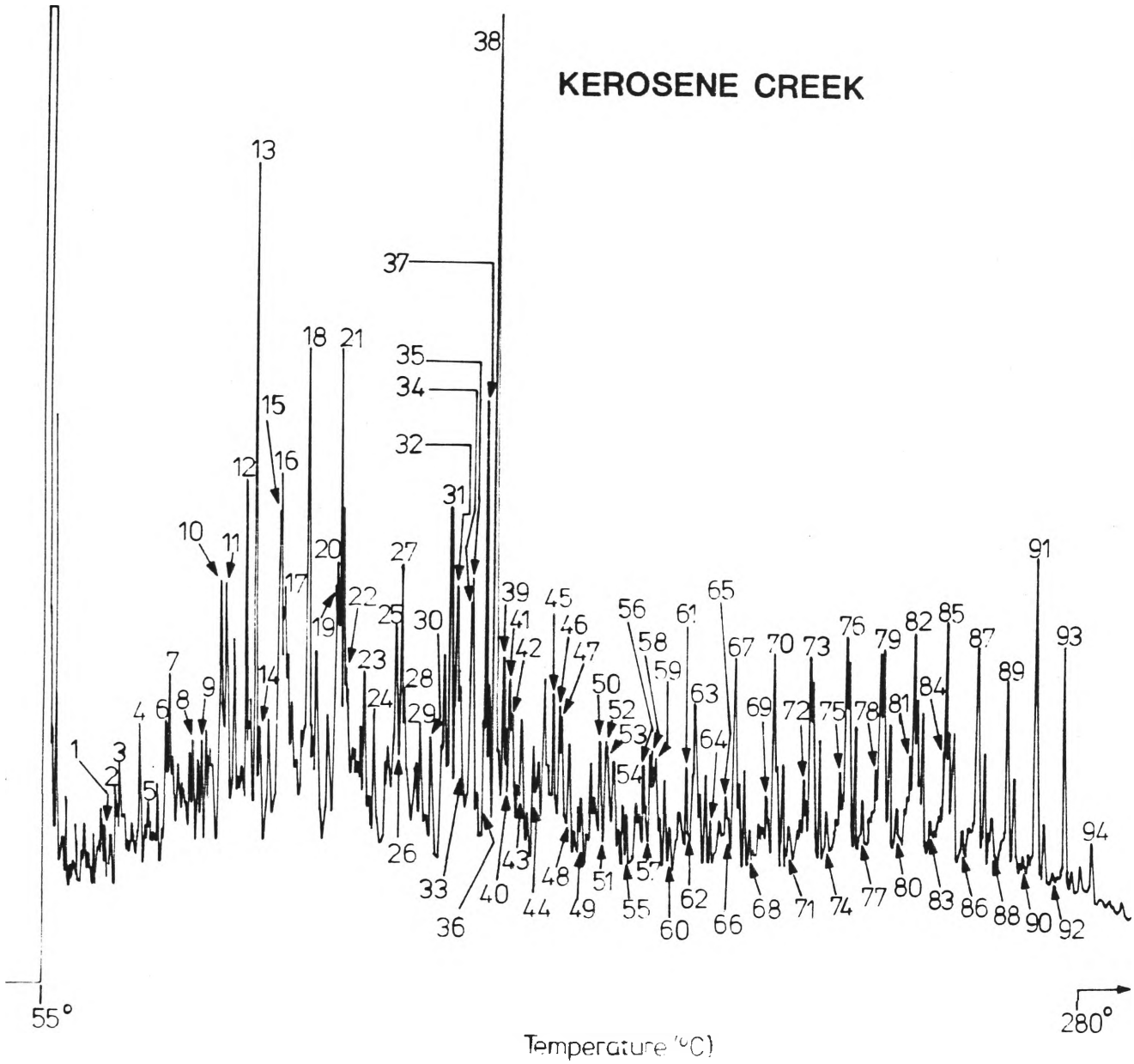


Figure 11. Gas chromatogram of the branched/cyclic alkene/alkylbenzene fraction from the Kerosene Creek shale oil. Numbers refer to compounds listed in Table 6.

Table 6. Branched/cyclic alkene and monosubstituted alkylbenzene fraction in the Fischer Assay and Lurgi oils

Peak No.[1]	Identity	Peak No.[1]	Identity
1	1-methyl-4-C_3cyclohexene	31	C_{11} cyclopentene
2	1-phenylpentane 2-phenylpentane C_5 cyclopentene	32	1-phenylundecane
3	n-C_4 cyclohex-1-ene	33	n-C_{10} cyclohex-1-ene
4	2-methyl-3-decene	34	2-methyl-3-hexadecene
5	1-methyl-4-C_4cyclohexene	35	pristene isomer
6	1-phenylhexane 2-phenylhexane C_6 cyclopentene	36	1-methyl-4-C_{10} cyclohexene
7	n-C_5cyclohex-1-ene	37	pristene isomer
8	2-methyl-3-undecene	38	pristene isomer
9	1-methyl-4-C_5cyclohexene	39	C_{12} cyclopentene
10	1-phenylheptane 2-phenylheptane C_7 cyclopentene	40	2-phenyldodecane
11	n-C_6 cyclohex-1-ene	41	1-phenyldodecane
12	2-methyl-3-dodecene	42	n-C_{11} cyclohex-1-ene
13	7-methyl-6-tridecene	43	2-methyl-3-heptadecene
14	1-methyl-4-C_6 cyclohexene	44	1-methyl-4-C_{11} cyclohexene
15	C_8 cyclopentene	45	C_{13} cyclopentene
16	1-phenyloctane 2-phenyloctane	46	1-phenyltridecane
17	n-C_7 cyclohex-1-ene	47	n-C_{12} cyclohex-1-ene
18	2-methyl-3-tridecene	48	2-methyl-3-octadecene
19	C_9 cyclopentene	49	1-methyl-4-C_{12} cyclohexene
20	2-phenylnonane	50	C_{14} cyclopentene
21	1-phenylnonane	51	2-phenyltetradecane
22	n-C_8 cyclohex-1-ene	52	1-phenyltetradecane
23	2-methyl-3-tetradecene	53	n-C_{13} cyclohex-1-ene
24	1-methyl-4-C_8 cyclohexene	54	2-methyl-3-nonadecene
25	C_{10} cyclopentene	55	1-methyl-4-C_{13} cyclohexene
26	2-phenyldecane	56	C_{15} cyclopentene
27	1-phenyldecane	57	2-phenylpentadecane
28	n-C_9 cyclohex-1-ene	58	1-phenylpentadecane
29	2-methyl-3-pentadecene	59	2-methyl-3-eicosene
30	1-methyl-4-C_9 cyclohexene	60	1-methyl-4-C_{14} cyclohexene
		61	C_{16} cyclopentene
		62	2-phenylhexadecane
		63	1-phenylhexadecane 2-methyl-3-heineicosene n-C_{15} cyclohex-1-ene

Table 6. continued

Peak[1] No.	Identity	Peak[1] No.	Identity
64	1-methyl-4-C_{15} cyclohexene	83	1-methyl-4-C_{21} cyclohexene
65	C_{17} cyclopentene	84	C_{23} cyclopentene 2-phenyltricosane
66	2-phenylheptadecane	85	1-phenyltricosane 2-methyl-3-octacosene n-C_{22} cyclohex-1-ene
67	n-C_{16} cyclohex-1-ene 2-methyl-3-docosene 1-phenylheptadecane	86	1-methyl-4-C_{22} cyclohexene
68	1-methyl-4-C_{16} cyclohexene	87	C_{24} cyclopentene 2-phenyltetracosane 1-phenyltetracosane 2-methyl-3-nonacosene n-C_{23} cyclohex-1-ene
69	C_{18} cyclopentene 2-phenyloctadecane	88	1-methyl-4-C_{23} cyclohexene
70	1-phenyloctadecane 2-methyl-3-tricosene n-C_{17} cyclohex-1-ene	89	C_{25}cyclopentene 2-phenylpentacosane 1-phenylpentacosane 2-methyl-3-triacontene n-C_{24} cyclohex-1-ene
71	1-methyl-4-C_{17} cyclohexene	90	1-methyl-4-C_{24} cyclohexene
72	C_{19} cyclopentene 2-phenylnonadecane	91	C_{26} cyclopentene 2-phenylhexacosane 1-phenylhexacosane 2-methyl-3-hentriacontene n-C_{25} cyclohex-1-ene
73	1-phenylnonadecane 2-methyl-3-tetracosene n-C_{18} cyclohex-1-ene	92	1-methyl-4-C_{25} cyclohexene
74	1-methyl-4-C_{18} cyclohexene	93	C_{27} cyclopentene 2-phenylheptacosane 1-phenylheptacosane 2-methyl-3-dotriacontene n-C_{26} cyclohex-1-ene
75	C_{20} cyclopentene 2-phenyleicosane		
76	1-phenyleicosane 2-methyl-3-pentacosene n-C_{19} cyclohex-1-ene		
77	1-methyl-4-C_{19} cyclohexene		
78	C_{21} cyclopentene 2-phenylheneicosane		
79	1-phenylheneicosane 2-methyl-3-hexacosene n-C_{20} cyclohex-1-ene		
80	1-methyl-4-C_{20} cyclohexene		
81	C_{22} cyclopentene 2-phenyldocosane		
82	1-phenyldocosane 2-methyl-3-heptacosene n-C_{21} cyclohex-1-ene		

(1) Numbers refer to peaks in Figures 11, 24 and D (Appendix)

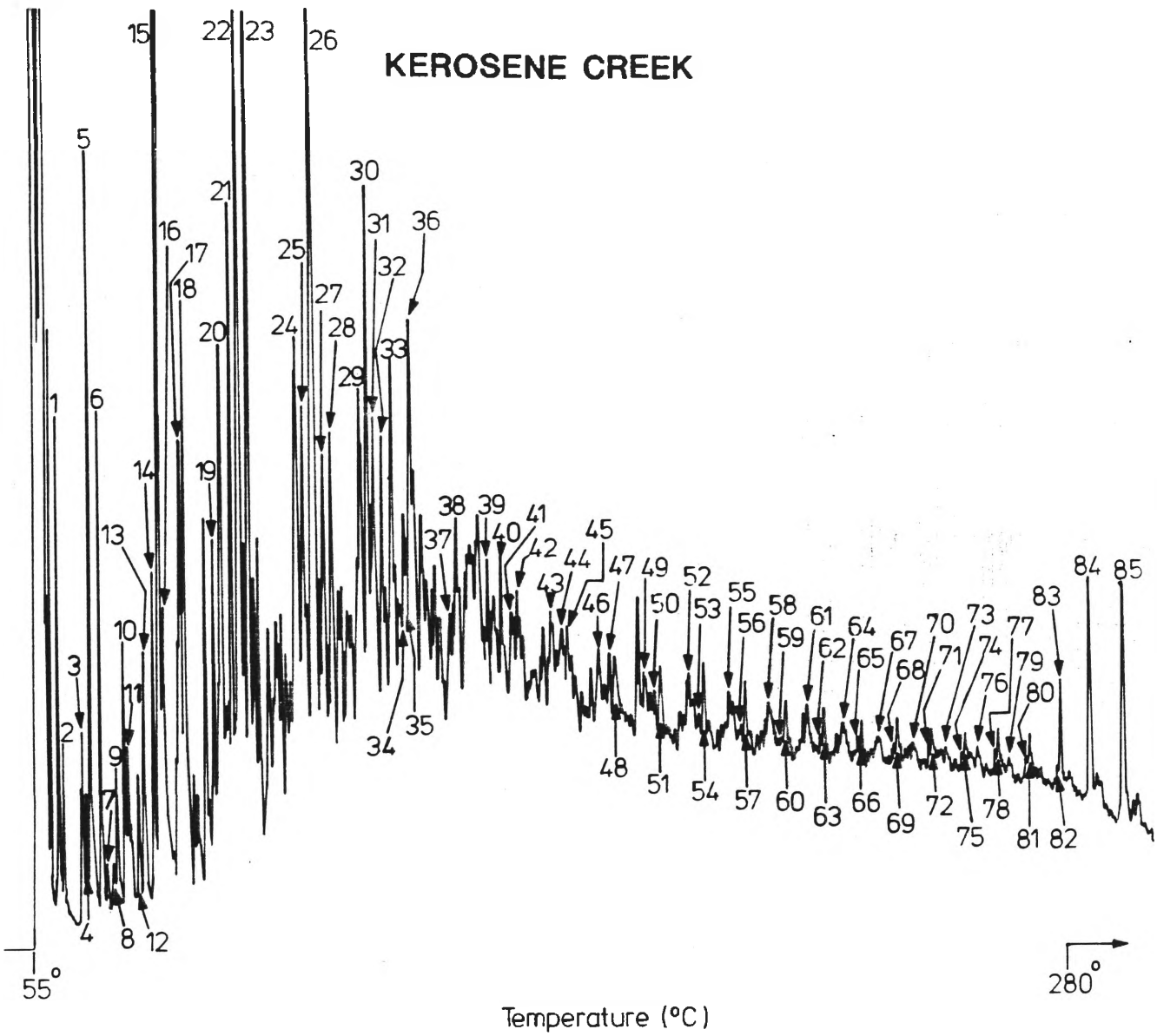


Figure 12. Gas chromatogram of the diaromatic fraction from the Kerosene Creek shale oil. Numbers refer to compounds listed in Table 7.

Table 7. Diaromatic fraction in the Fischer Assay and Lurgi oils

Peak No.[1]	Identity	Peak No.[1]	Identity
1	m or p-xylene	40	1-phenylundec-4-ene
2	o-xylene	41	2-C_6 naphthalene
3	1,3,5-trimethylbenzene	42	1-C_6 naphthalene
4	1,3,4-trimethylbenzene	43	1-phenyldodec-4-ene
5	1,2,4-trimethylbenzene	44	2-C_7 naphthalene
6	1,2,3-trimethylbenzene	45	1-C_7 naphthalene
7	indan	46	1-phenyltridec-4-ene
8	indene	47	2-C_8 naphthalene
9	dimethylethylbenzene	48	1-C_8 naphthalene
10	1,3-dimethyl-4-ethyl-benzene	49	1-phenyltetradec-4-ene
11	1,3-dimethyl-2-ethyl-benzene	50	2-C_9 naphthalene
12	1,4-dimethyl-2-ethyl-benzene	51	1-C_9 naphthalene
13	tetramethylbenzene	52	1-phenylpentadec-4-ene
14	4 or 5-methylindan	53	2-C_{10} naphthalene
15	1 or 2-methylindan, 1-methyl-1H-indene	54	1-C_{10} naphthalene
16	tetramethylbenzene	55	1-phenylhexadec-4-ene
17	naphthalene	56	2-C_{11} naphthalene
18	4,6 or 4,7 or 5,6-dimethylindan	57	1-C_{11} naphthalene
19	1,1 or 1,2 or 1,3-dimethylindan	58	1-phenylheptadec-4-ene
20, 21	4,6 or 4,7 or 5,6-dimethylindan	59	2-C_{12} naphthalene
22	2-methylnaphthalene	60	1-C_{12} naphthalene
23	1-methylnaphthalene	61	1-phenyloctadec-4-ene
24	6-methyl-1,2-dihydro-naphthalene	62	2-C_{13} naphthalene
25	1,3-dimethylnaphthalene	63	1-C_{13} naphthalene
26	1-ethylnaphthalene	64	1-phenylnonadec-4-ene
27, 28	dimethylnaphthalene isomers	65	2-C_{14} naphthalene
29	isopropylnaphthalene	66	1-C_{14} naphthalene
30, 31, 32, 33	trimethylnaphthalene isomers	67	1-phenyleicos-4-ene
34	2-butylnaphthalene	68	2-C_{15} naphthalene
35	3 or 4-methylbiphenyl	69	1-C_{15} naphthalene
36	1-butylnaphthalene	70	1-phenylheineicos-4-ene
37	2-C_5 naphthalene	71	2-C_{16} naphthalene
38	1-C_5 naphthalene	72	1-C_{16} naphthalene
39	2,4-dimethylbiphenyl	73	1-phenyldocos-4-ene
		74	2-C_{17} naphthalene

Table 7. continued

Peak No.[1]	Identity
75	1-C_{17} naphthalene
76	1-phenyltricos-4-ene
77	2-C_{18} naphthalene
78	1-C_{18} naphthalene
79	1-phenyltetracos-4-ene
80	2-C_{19} naphthalene
81	1-C_{19} naphthalene
82	2-C_{20} naphthalene
83	1-C_{20} naphthalene
84	1-C_{21} naphthalene 2-C_{21} naphthalene
85	1-C_{22} naphthalene 2-C_{22} naphthalene

(1) Numbers refer to peaks in Figures 12, 25 and E (Appendix)

2-alkylnaphthalenes (C_1 - C_{22} alkyl chains) and 1-phenyl-4-alkenes (Table 7). Trimethylbenzenes, polysubstituted indans, methylnaphthalenes and ethylnaphthalene were the most abundant aromatic compounds in the diaromatic fraction in all the shale oils from the Rundle deposit (Figure E; Appendix). Alkylnaphthalenes may be derived from dehydrogenation of cyclic sesquiterpenes (Streibl and Herout, 1969). The Ramsay Crossing shale oil contains a prominent homologous series of 2-phenyl-3,4-dimethylalkanes (linear chain C_{12} - C_{24}) as indicated by the letter 'a' in Figure E (Appendix). These compounds are characterized by having diagnostic mass spectral ions (in order of decreasing intensities): m/e 57, 105, 71, 106, 85, 55, 69, 83. These compounds do not appear in the other oils.

The polyaromatic hydrocarbon fraction which constitutes 4 - 5% in each oil (Table 4) contains aromatic compounds with 3 - 5 rings and their partially hydrogenated derivatives (Table 8). Figure 13 represents a typical gas chromatogram of the polyaromatic hydrocarbon fraction. Fluorene, substituted fluorenes and phenanthrenes were the dominant compounds in this fraction. The relative abundance of polyaromatic compounds decreases with increasing ring number. Aromatic compounds with greater than 6 fused rings may be present but they are not sufficiently volatile for analysis by g.c. The polyaromatic hydrocarbons in the oils from the various stratigraphic seams were similar except that in the Munduran Creek shale oil the ratio of phenanthrene to anthracene is 5:1 whereas in the other oils the ratio is about 2:1 (Figure F; Appendix). Polyaromatic hydrocarbons may arise from the oxidation or dehydrogenation of steroids

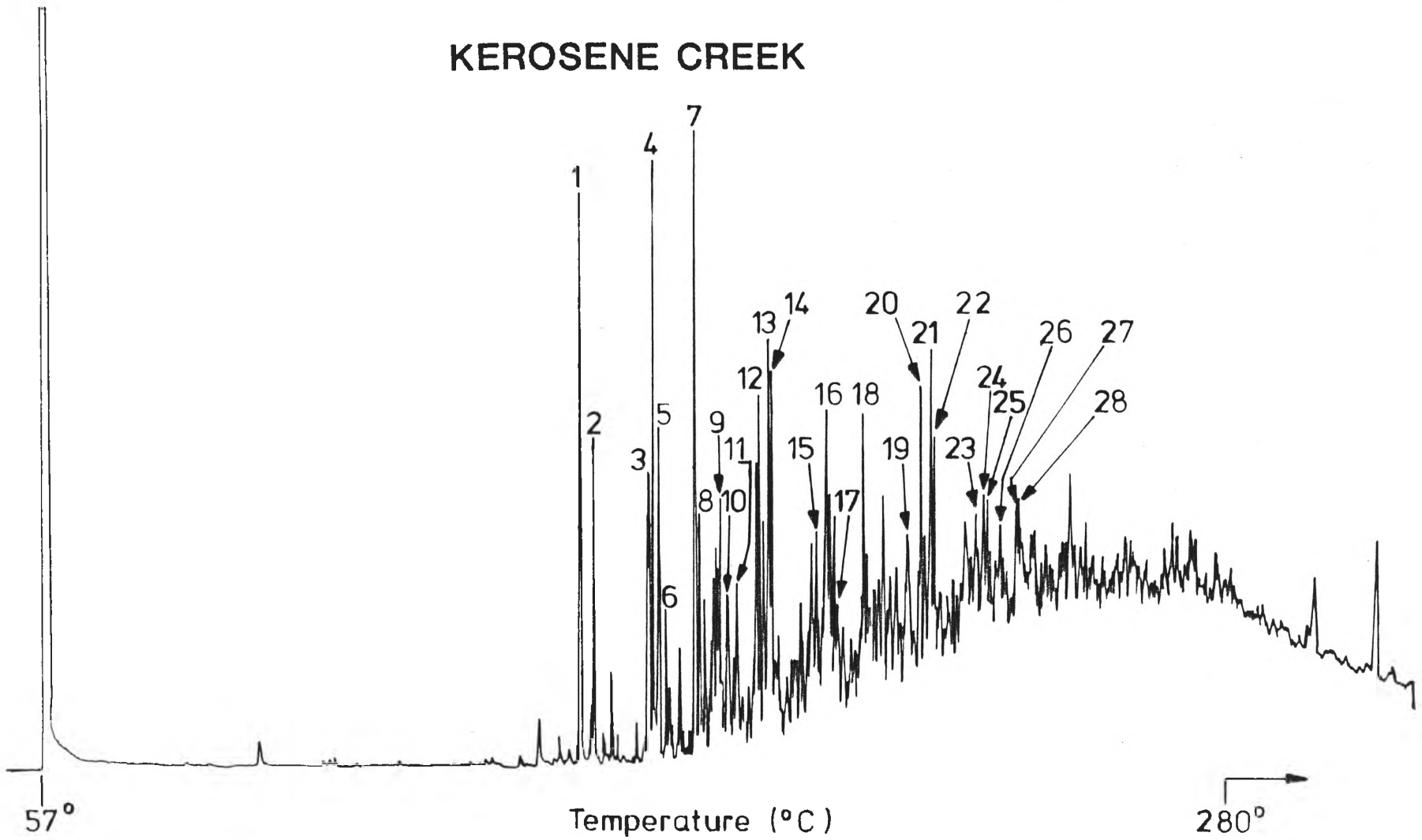


Figure 13. Gas chromatogrm of the polyaromatic fraction from the Kerosene Creek shale oil. Numbers refer to compounds listed in Table 8.

Table 8. Polyaromatic hydrocarbon fraction in the Fischer Assay and Lurgi oils

Peak No. (1)	Identity
1	fluorene
2	9-methylfluorene
3, 4, 5	methylfluorene isomers
6	dimethylfluorene
7	phenanthrene
8	anthracene
9, 10	ethylfluorene
11	dimethylfluorene
12, 13, 14	methylphenanthrene isomers
15, 16	dimethylphenanthrene isomers
17	fluoranthene
18	pyrene
19	1,2-benzofluorene
20	2,3-benzofluorene
21, 22	methylpyrene isomers
23, 24, 25, 26	ethylpyrene and/or ethylfluoranthene
27	1,2-benzanthracene or naphthacene
28	triphenylene or chrysene

(1) Numbers refer to peaks in Figures 13, 26 and F (Appendix)

and triterpenoids during pyrolysis.

D) Nitriles

The aliphatic nitriles in the Kerosene Creek oil ranged from C_9 to C_{34} with maxima at C_{18} and C_{28} and strong even carbon number preference in the region C_{22} - C_{34} (Figure 14). The distribution of aliphatic nitriles is similar in the other oils (Figure G; Appendix). Nitriles have been detected previously in shale oil (Iida et al., 1966; Regtop et al., 1982) but their origin has not yet been definitely established. The nitrile group has high thermodynamic stability and could be derived from the dehydration of amides (Finar, 1967). An origin from heterocyclic aromatics is unlikely because of the stability conferred on these compounds by the aromatic ring structure (Finar, 1967). There appear to be a number of nitrile precursors in the kerogen: the bimodal nitrile envelope suggests separate algal and higher plant sources and the even carbon number preference near the C_{28} maximum indicates a pyrolysis mechanism which retains the biological bias for compounds with even carbon numbers (Parker, 1969). The aliphatic nitrile fraction constitutes 6 - 13% of the total oils (Table 4).

E) Ketones

Methyl ketones are the dominant ketones in the Rundle shale oils. Kerosene Creek shale oil has a homologous series of methyl ketones ranging from C_9 to C_{33}, maxima at C_{19} and C_{29} and odd carbon number preference in the region C_{25} - C_{32} (Figure 15). The C_{19} maximum is larger than the C_{29} maximum. The distribution of methyl ketones in the other oils was similar except that in Brick Kiln, Munduran Creek

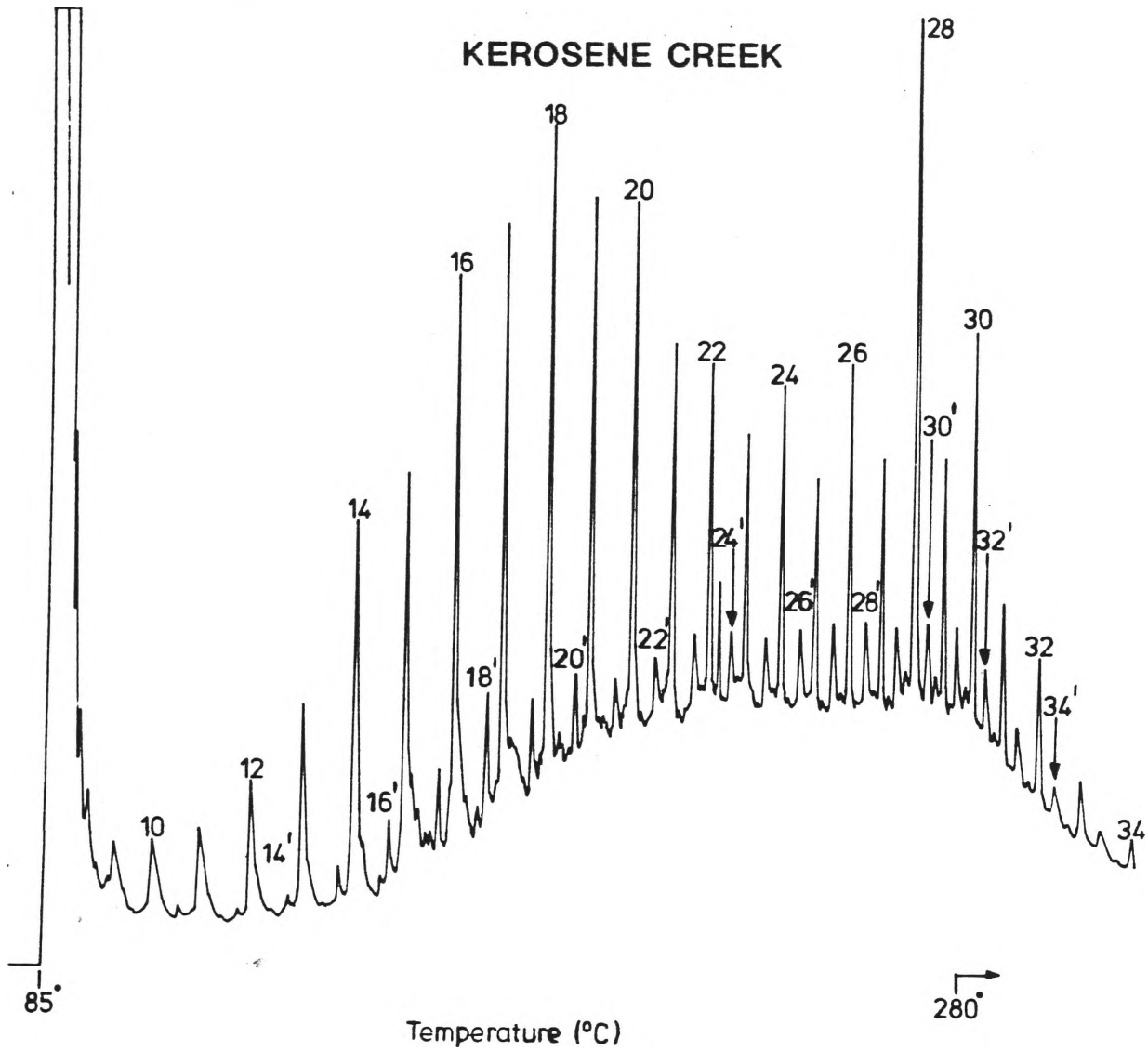


Figure 14. Gas chromatogram of the nitrile fraction from the Kerosene Creek shale oil. Carbon numbers are indicated for homologous straight-chain alkylnitriles (no prime) and 6-alkanones (with prime).

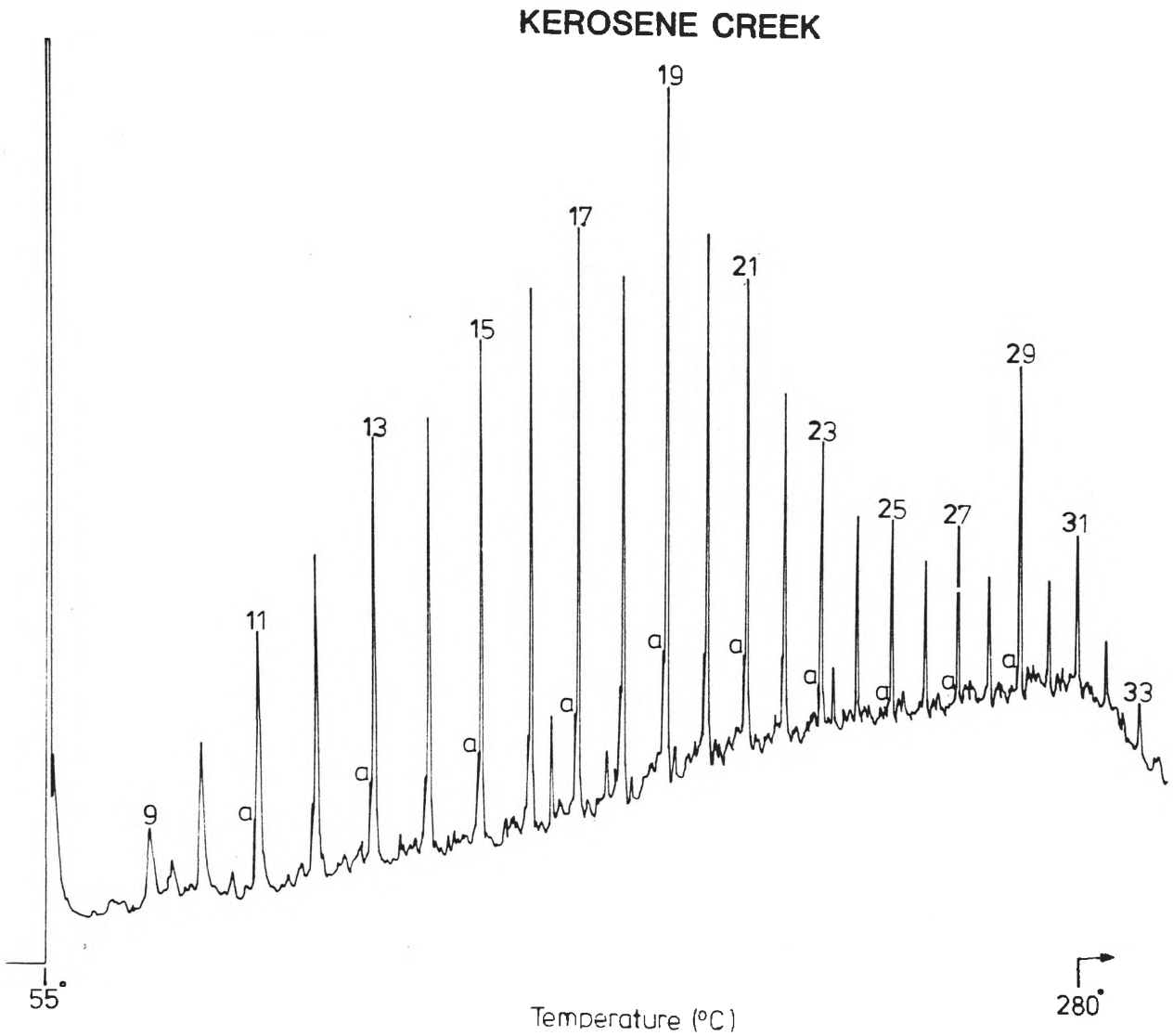


Figure 15. Gas chromatogram of the methyl ketone fraction from the Kerosene Creek shale oil. Carbon numbers of homologous 2-alkanones are indicated. a denotes a series of homologous unsaturated straight-chain methyl ketones.

and Humpy Creek oil the C_{29} maximum is larger than the C_{19} maximum. In the Ramsay Crossing shale oil, there is a maximum at C_{17} and there are no methyl ketones above C_{25} (Figure H; Appendix). In all the oils, the g.c. peaks of the methyl ketones are preceded by smaller peaks on the shoulder and the mass spectral fragmentation of these peaks suggests that they may be aliphatic unsaturated methyl ketones. The molecular weights of these compounds are two less than the methyl ketones and have the following characteristic mass spectral ions (in order of decreasing intensities): m/e 43 (base peak), 58, 41, 44, 71, 59, 82, M-33, M-18. The retention times for these aliphatic unsaturated methyl ketones on the g.c. column in the Brick Kiln shale oil are slightly different from the rest of the oils because of the degradation of the g.c. column at the time. In the nitrile fractions (Figure 14, G) there is another homologous series which according to the mass spectra appears to be a series of 6-alkanones ranging from C_{12} to C_{34}. These have not been reported previously in shale oil. The methyl ketone fraction constitutes 8 - 10% of the total oil, but this fraction also contains a brown polymeric material.

The bimodal distribution pattern indicates separate algal and higher plant sources similar to the nitrile distribution. An odd carbon number preference is indicative of a biological precursor with a likely pathway being the β-oxidation of fatty acids followed by decarboxylation of the resultant β-keto acid (Davis, 1967). Alternatively thermolysis of β-ketoester under acidic conditions gives an alcohol plus a 2-alkanone and carbon dioxide (March, 1968). At the

retort temperature the alcohol would dehydrate to a 1-alkene.

F) Amides

The amide fraction of the Kerosene Creek oil (Figure 16) contained homologous series of straight-chain alkanamides and 2-methylalkanamides ranging from C_9 to C_{28}. The alkanamides have a maximum at C_{22} whereas the 2-methyl-alkanamides at C_{18}. Amides were first reported in shale oil by Regtop et al. (1982). Amides dehydrate easily to yield nitriles (Finar, 1967) and represent possible precursors of these compounds. The Munduran Creek, Brick Kiln and Humpy Creek shale oils have similar distribution of amides except that they have a bimodal distribution of alkanamides with maxima at C_{20} and C_{28} and even carbon number preference in the region C_{24} - C_{28} (Figure I; Appendix). The C_{28} is the dominant alkanamide. This distribution is similar to the aliphatic nitriles. The chromatographic fraction of the Ramsay Crossing oil is a complex and poorly-resolved mixture in which amides were not detected. It is likely that amides, perhaps present originally in the kerogen, are precursors of some of the nitriles. The amide fraction constitutes 3 - 5% of the oils (Table 4) and also contains a brown polymeric material, which, by looking at the unresolved envelope in the g.c. profiles of the amide fractions, constitutes the bulk of the amide fraction. The characteristic mass spectral ions for alkanamides are m/e 59 (base peak), 72 and for 2-methylalkanamides m/e 73 (base peak), 86.

G) Acidic and basic compounds

The compounds present in the acidic and basic fractions are reminiscent of those found in coal tar. The

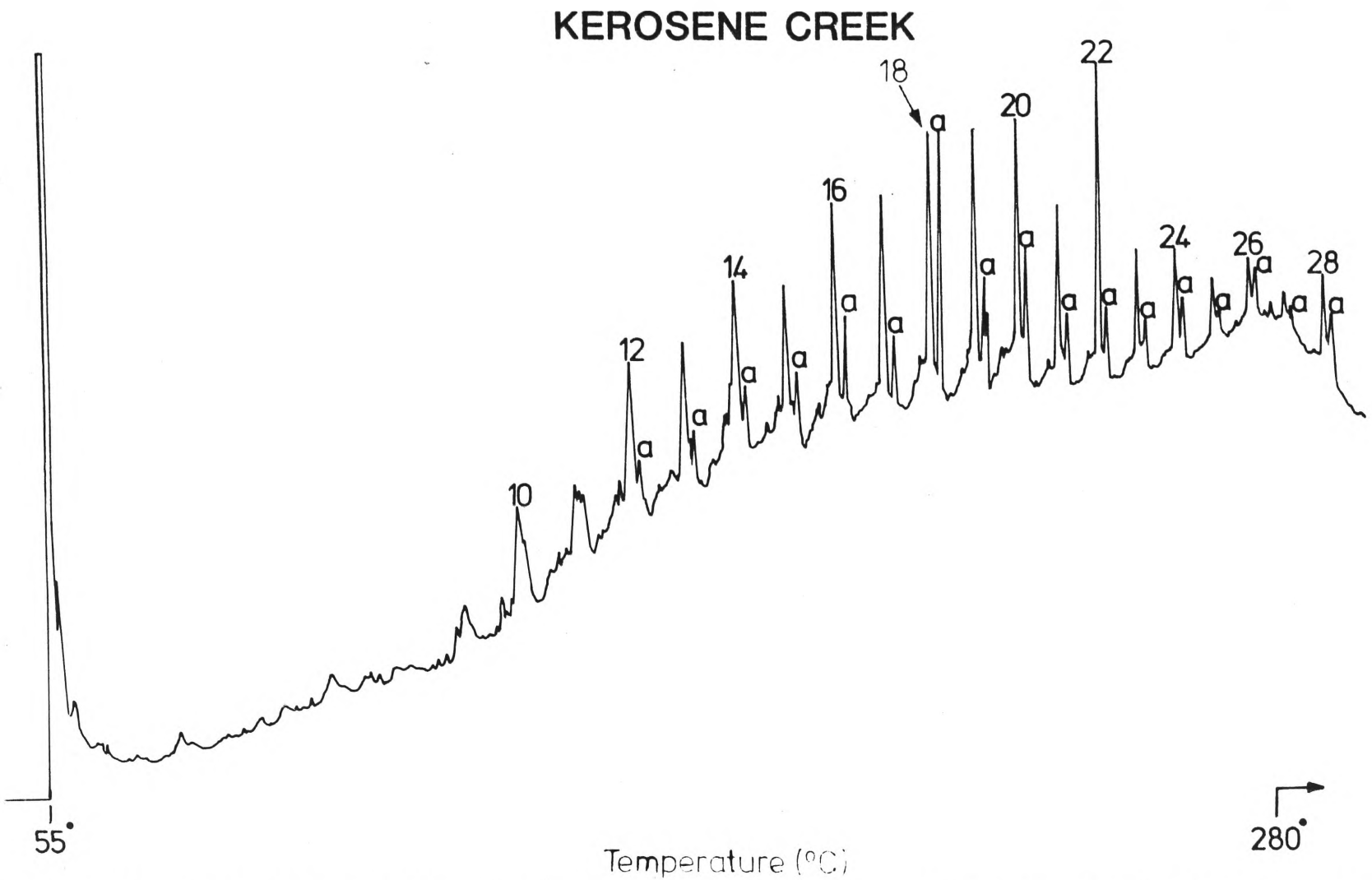


Figure 16. Gas chromatogram of the amide fraction from the Kerosene Creek shale oil. a denotes a series of homologous 2-methylalkanamides. Carbon numbers of homologous straight-chain alkanamides are indicated.

acidic fraction can be divided into a phenolic fraction and carboxylic acids. The total acidic fraction constitutes 2 to 3% of the total oil (Table 4). The phenolic fraction of the Kerosene Creek oil (Figure 17) contained predominantly phenol, o- and m-cresol, di-and trimethylphenols. Naphthols were also found but in small amounts (Table 9). The other oils have similar g.c. profiles except that in Ramsay Crossing oil the dominant compound is o-cresol whereas m-cresol is dominant in the rest of the oils (Figure J; Appendix). Phenols are widely distributed in the plant kingdom and in particular are structural elements of lignins (land plants) and tannins (algae and land plants) (Tissot and Welte, 1978c).

The carboxylic acids constitute only a small portion of the acidic fraction (approximately less than 0.5% of the total oil). Figure 18, represents the g.c. profile of the methyl-ester derivatives of aliphatic carboxylic acids in the Kerosene Creek oil. The carboxylic acids range from C_6 to C_{18}, with the majority of the acids in the region C_6 to C_{11} and a maximum at C_9. The acids in the region C_{12} - C_{18} occur in trace amounts with even carbon number preference. The g.c. profiles of carboxylic acids are similar for all the oils (Figure K; Appendix). It is most likely that some of the lower molecular weight acids (less than C_8) would be lost by volatilisation and by partitioning into the retort waters and therefore the apparent C_9 maximum may not be correct.

The basic fraction, which constitutes 2 - 3% of the total oil from the Rundle deposit, is a more complex mixture than the acidic fraction. The basic fraction of the Kerosene Creek oil contained predominantly substituted pyridines, quinolines

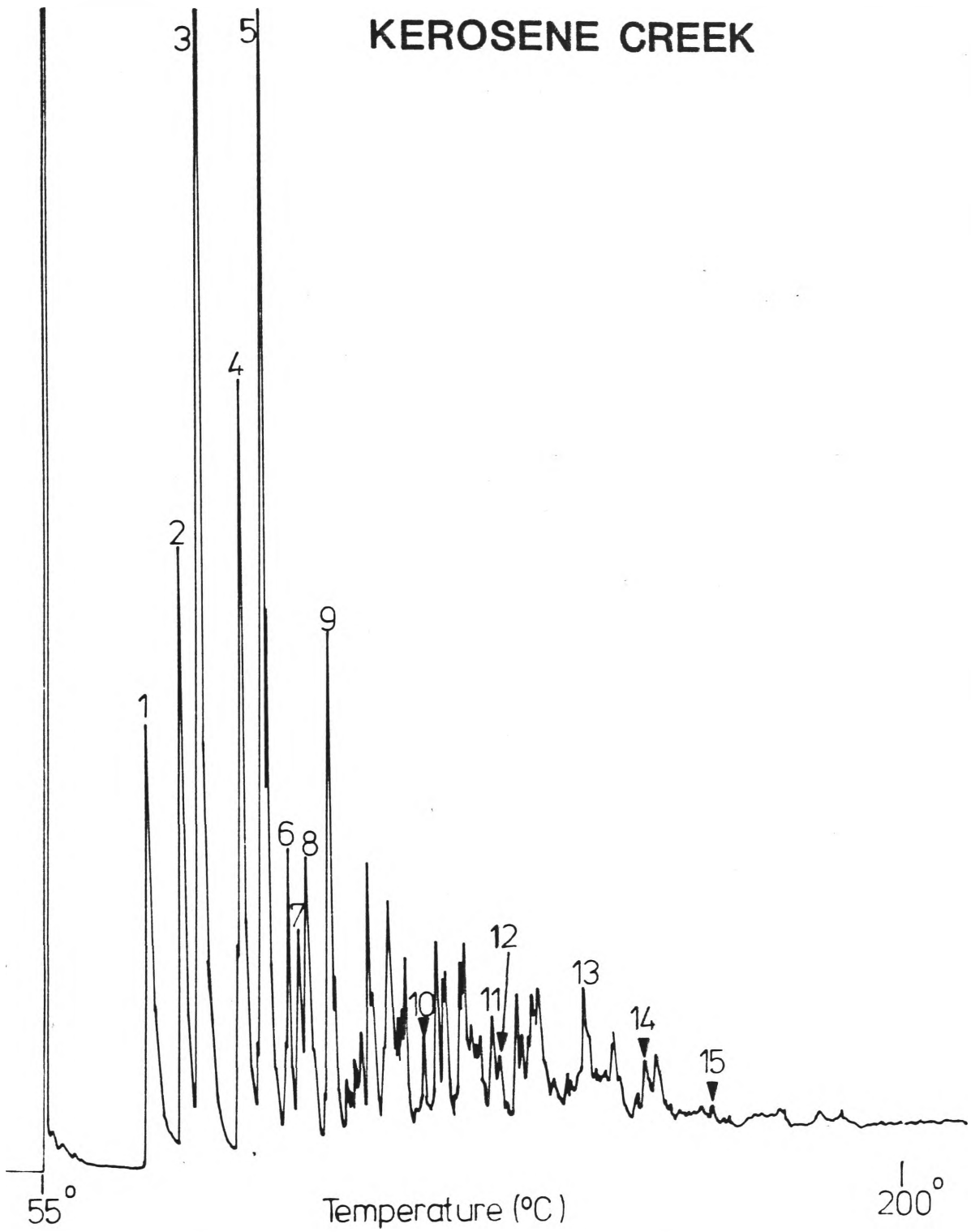


Figure 17. Gas chromatogram of the phenolic fraction (acidic) from the Kerosene Creek shale oil. Numbers refer to compounds listed in Table 9.

Table 9. Phenolic compounds identified in the Fischer Assay oils

Peak No.[1]	Identity
1	phenol
2	o-cresol
3	m-cresol
4	2,6-dimethylphenol
5	2,4 or 2,5-dimethylphenol
6	2,3-dimethylphenol
7	trimethylphenol
8	3-ethyl-5-methylphenol
9	trimethylphenol
10	o-methylallylphenol
11, 12	dimethylallylphenol isomers
13	2 or 3-methyl-1-naphthol
14, 15	dimethylnaphthol isomers

(1) Numbers refer to peaks in Figures 17 and J (Appendix)

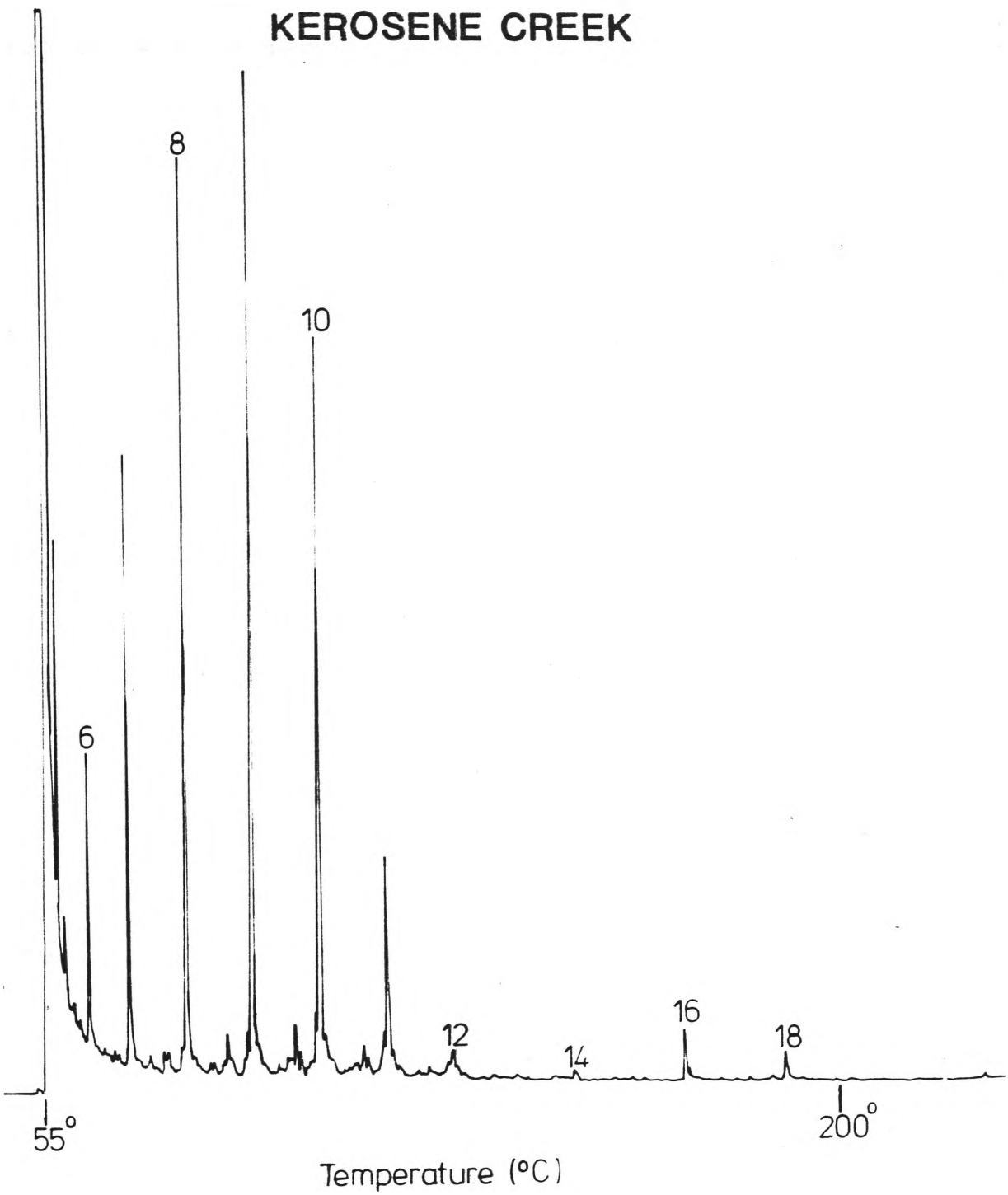


Figure 18. Gas chromatogram of the methyl ester derivatives of aliphatic carboxylic acids from the Kerosene Creek shale oil. Carbon numbers are indicated.

and tetrahydroquinolines with minor amounts of acridines (Figure 19; Table 10). The g.c. profiles of the other oils from the Rundle deposit were similar (Figure L; Appendix). An unknown compound, labelled with the letter "a" in the g.c. profiles, was abundant in the Kerosene Creek oil but occurred in trace amounts in the other oils from the Rundle deposit. This unknown compound has the following characteristic mass spetral ions: m/e 67 (base peak), 110, 163 (M^+). Proteins and nucleic acids are presumed to be the original sources of most nitrogen heterocycles in shale oil (Mapstone, 1951). Due to their deleterious effect on fuel stability (Brown and Karn, 1980), catalyst lifetime (Mills et al., 1950) and the potential adverse health and environmental impact (Ho et al., 1979), nitrogen heterocycles are of considerable importance.

H) Polymeric material

A significant amount of polymeric material was found in the shale oils. The acidic and basic extractions were effective in catalysing polymerisation reactions. The amount of tar (polymeric material) obtained due to acidic and basic extractions was 6 - 11% of the total oil (Table 4). It has been reported that solvent extraction and partitioning of polar compounds can cause formation of tar and stable emulsion (Clark et al., 1975). Also it is known that shale oil polymerises rapidly on contact with light and air causing the oil to become more viscous.

A free-radical mechanism is an obvious choice for the mechanism of this oxidative degradation. Autoxidation of organic substances through a free-radical mechanism is well

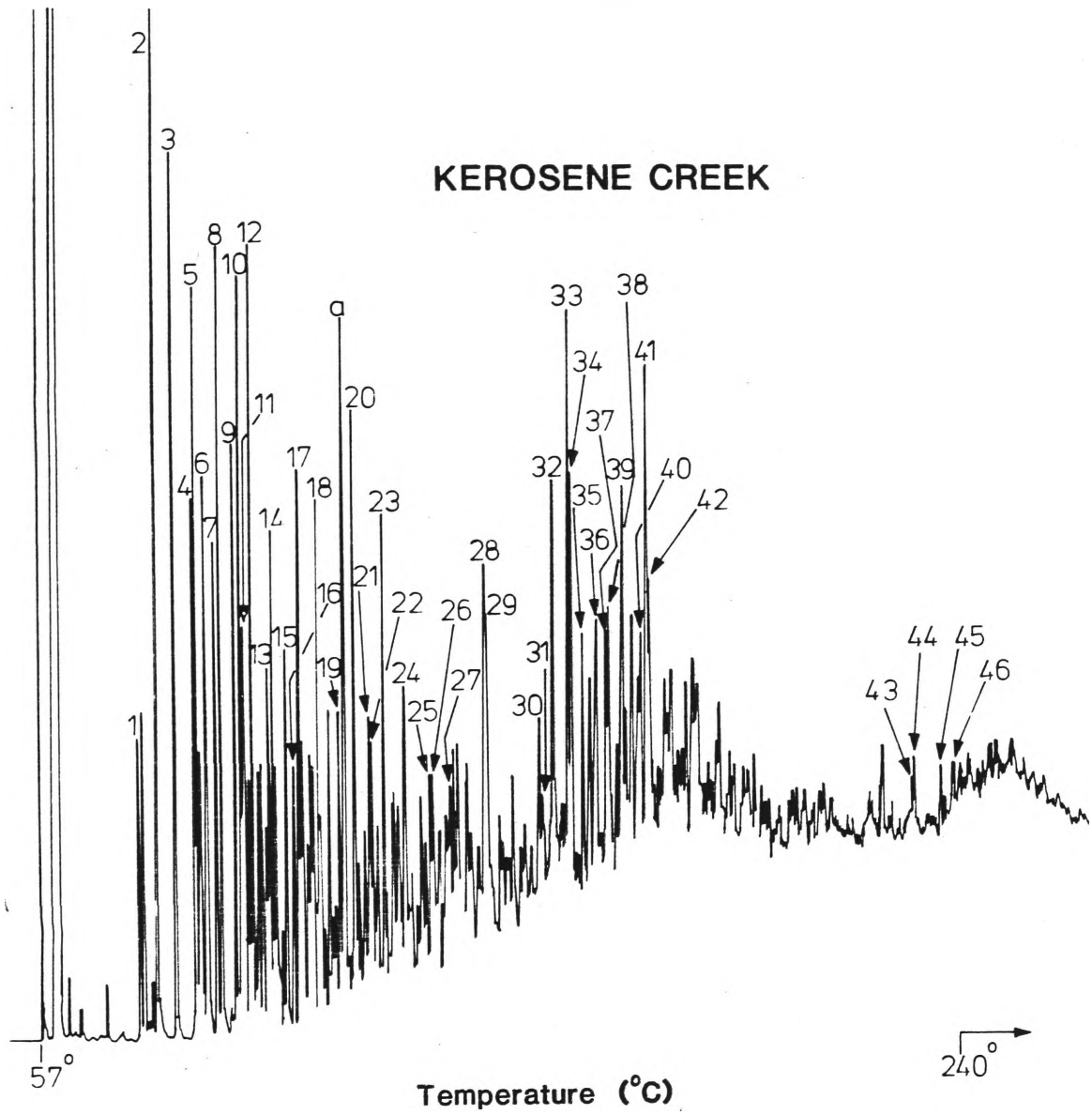


Figure 19. The gas chromatogram of the basic fraction from the Kerosene Creek shale oil. Numbers refer to compounds listed in Table 10.

Table 10. Basic fraction in the Fischer Assay and Lurgi oils

Peak No.[1]	Identity[2]	Peak No.[1]	Identity[2]
1	pyridine	25	C_7 substituted pyridine (m/e 107*, M^+ 177)
2	2 or 4-methylpyridine		
3	2,3-dimethylpyridine	26	C_7 substituted pyridine (m/e 93*, M^+ 177)
4	2-ethylpyridine		
5	3-methylpyridine	27	5,6,7,8-tetrahydro-quinoline
6	2-methyl-6-ethyl-pyridine		
7	2,5-dimethypyridine	28	C_8 substituted pyridine (m/e 107*, M^+ 191)
8	3,4 or 3,5-dimethyl-pyridine		
9	2,3-dimethylpyridine	29	C_8 substituted pyridine (m/e 93*, M^+ 191)
10	2,4,6-trimethylpyridine		
11	3-ethylpyridine	30	C_9 substituted pyridine (m/e 107*, M^+ 205)
12	trimethylpyridine		
13	3-ethyl-5-methyl-pyridine	31	C_9 substituted pyridine (m/e 93*, M^+ 205)
14	2,4-dimethyl-6-ethyl-pyridine	32	quinoline
15	dimethylethylpyridine	33	2-methylquinoline
16	2,6-dimethyl-4-ethyl-pyridine	34	8-ethylquinoline
		35	3-methylquinoline
17	C_5 substituted pyridine (m/e 107*, M^+ 149)	36	methylquinoline
		37	4-ethylquinoline
18	C_5 substituted pyridine (m/e 121*, M^+ 149)	38	methylquinoline
		39	2,6-dimethylquinoline
19	C_6 substituted pyridine (m/e 121*, M^+ 163)	40	2,4-dimethylquinoline
		41	propylquinoline
20	dimethylethylpyridine	42	3-ethylquinoline
21	C_6 substituted pyridine (m/e 107*, M^+ 163)	43	acridine or 7,8-benzoquinoline
		44	methylbenzoquinoline
22	C_6 substituted pyridine (m/e 93*, M^+ 163)	45	acridine or 7,8-benzoquinoline
		46	methylbenzoquinoline
23	indoline	a	m/e 67*, 110, M^+ 163
24	1,2,3,4-tetrahydro-quinoline		

(1) Numbers refer to peaks in Figures 19, 31 and L (Appendix)

(2) Electron impact ionization: asterisk indicates base peak

known and widely studied. Basically the process involves radical initiation, propagation, branching and termination. If the propagation step of the autoxidation can be stopped, the deleterious impact of the oxidation can be avoided. One method to terminate the chain reaction is to have the free radicals, which are generated, react with a substance forming a stable compound. Phenols are such propagation inhibitors, because the resulting free radical is resonance-stabilized and thus less susceptible to further oxidation (Reich and Strivala, 1969). Shale oil has an appreciable concentration of phenols, but the question arises as to why the oil polymerises even in the presence of these inhibitors. It may be possible that the phenols present are not of the correct structure to either make them available for reaction with free radicals or to stabilize them after such reactions. Also, if there is a high initial concentration of free radicals, many reactions in the chain mechanism may occur before any potential inhibitor has the opportunity to terminate the chain.

The shale oil samples from the Rundle deposit were at least 2 years old before analysis and no precautions were taken to protect the oils from air and light. Ingram et al. (1983) analysed a freshly retorted shale oil by g.c. - m.s. from the Kerosene Creek seam of the Rundle deposit and it appeared that there was little difference in the volatile components of the oil as compared with the aged shale oil, except that the amount of tar formed after acidic and basic extractions in the freshly retorted oil was 1.5% as compared with 11.4% in the aged oil, using the same procedure.

The neutral fractions, after acidic and basic extractions contained (or formed) a substantial amount of brown polymeric material which was eluted from the open column with chloroform and methanol.

The shale oils contained a significant amount of asphaltenes (2 - 4% of the total oil). The asphaltenes gave no detectable aromatic proton signal by n.m.r. (Regtop et al., 1982) and are believed to be high molecular weight polymers of largely aliphatic material.

This research only involved the analysis of g.c. volatile components and no attempt was made to investigate the non-volatile (polymer) portion of the shale oils. Future research should involve the characterization of non-volatile polymers by techniques such as pyrolysis - gas chromatography - mass spectrometry (g.c./m.s.).

2. Lurgi-Ruhrgas process

The Lurgi oils, which include light, middle and heavy oil are highly aliphatic in character (H/C = 1.5 - 1.6; Table 11). The temperature ranges at which the various fractions were collected by the Lurgi-Ruhrgas process and the approximate percentages of the oil fractions in the total oil are as follows: (1) 220^{o} - 520^{o}C, heavy oil, 20%; (2) 200^{o} - 480^{o}C, middle oil, 13%; (3) 70^{o} - 360^{o}C, light oil, 67%; (4) 20^{o} - 150^{o}C, naphtha, 10%. These figures were supplied by Southern Pacific Petroleum. The naphtha fraction was not available and therefore not analysed.

The procedure for the open column chromatography of the Lurgi oils was similar to that of the Fischer Assay oils except that the amount of neutral fraction applied to the open chromatographic column was less for the Lurgi oils. It was found that if the amount of neutral fraction applied to the open chromatographic column for the Lurgi oils was the same as for the Fischer Assay oils, even though the alkanes and alkenes separated, the aliphatic nitriles tended to remain longer on the column for the Lurgi oils than for the Fischer Assay oils when eluting with dichloromethane. Therefore, incomplete separation of nitriles and methyl ketones occurred. The aliphatic nitriles in the Lurgi oils required a larger volume of dichloromethane for elution than did a similar column loading of Fischer Assay oils. However, by applying less neutral fraction of the Lurgi oils to the column, the aliphatic nitriles eluted more quickly off the column (i.e. within the same volume as for the Fischer Assay oils). Also the methyl ketones eluted directly after the nitriles using

Table 11. Elemental composition of the Lurgi oils

Shale oil	% element in oil[a]					H/C
	C	H	N	S	O	
Light oil	85.2	11.6	1.4	0.7	1.2	1.6
Middle oil	85.4	10.9	1.2	0.3	1.2	1.5
Heavy oil	85.3	10.8	1.2	0.5	1.2	1.5

a Analyses were performed by the Australian Mineral Development Laboratories, Microanalytical Service

dichloromethane, whereas in the Fischer Assay oils the methyl ketones remained longer on the column and needed chloroform for elution.

A) Alkanes

The carbon distribution and the percentage of straight-chain alkanes in each Lurgi oil are as follows: (1) light oil: C_8 - C_{24}, maximum at C_9, 10.8% n-alkanes; (2) middle oil: C_9 - C_{33}, maxima at C_{18} and C_{27} (C_{18} most abundant n-alkane) with odd carbon number preference in the region C_{23} - C_{27}, 12.8% n-alkanes; (3) heavy oil: C_{10} - C_{33}, maxima at C_{21} and C_{27} (C_{27} most abundant n-alkane) with odd carbon number preference in the region C_{21} - C_{27}, 12.3% n-alkanes (Figure 20, Table 12). The range of n-alkanes (C_8 - C_{33}) corresponds to that of the Fischer Assay oils (Figures 7, A). Since the light oil constitutes 67% of the total Lurgi oil, the straight-chain alkanes in the Lurgi oil are predominantly low molecular weight. Overall, the straight-chain alkanes constitute 11% of the total Lurgi oil as compared with 23% for the Fischer Assay oil from Kerosene Creek seam (Table 4). The slight odd carbon number preference in the middle and heavy oil is attributable to alkanes (found in higher plant waxes) which are derived biologically from the decarboxylation of fatty acids with even carbon numbers. This biological bias has survived the pyrolysis of the organic matter.

Branched/cyclic alkanes constitute 4% of the Lurgi light oil and comprise predominantly isoprenoid alkanes ranging from C_{13} - C_{16} and C_{18} - C_{20}, with C_{13} the dominant compound in this fraction (Figure 21). Minor amounts of 2- and 3-methyl-alkanes (C_{10} - C_{17}), alkylcyclohexanes (C_4 - C_{10} alkyl chain)

Table 12. Gravimetric results for the Lurgi oil fractions

Fraction[a]	Percentage mass		
	Light oil	Middle oil	Heavy oil
Asphaltene	0.8	3.0	6.1
Acidic	1.2	2.1	0.8
Basic	5.9	2.8	2.0
Tar	1.5	3.0	3.0
Linear alkane[b]	10.8	12.8	12.3
Branched/cyclic alkane	4.3	3.1	4.1
Linear alkene[b]	21.2	14.9	15.0
Branched/cyclic alkene and alkylbenzene	9.1	7.7	5.9
Diaromatic	15.3	10.7	10.6
Polyaromatic	5.0	11.1	11.0
Aliphatic nitrile	5.9	5.3	5.8
Methyl ketone	4.6	5.3	5.6
Polymeric	8.4	16.0	16.0
Methyl ester	5.4	6.0	6.0

a Fractions are named according to the most conspicuous compounds present

b These fractions are determined by difference between total and branched/cyclic material using molecular sieve

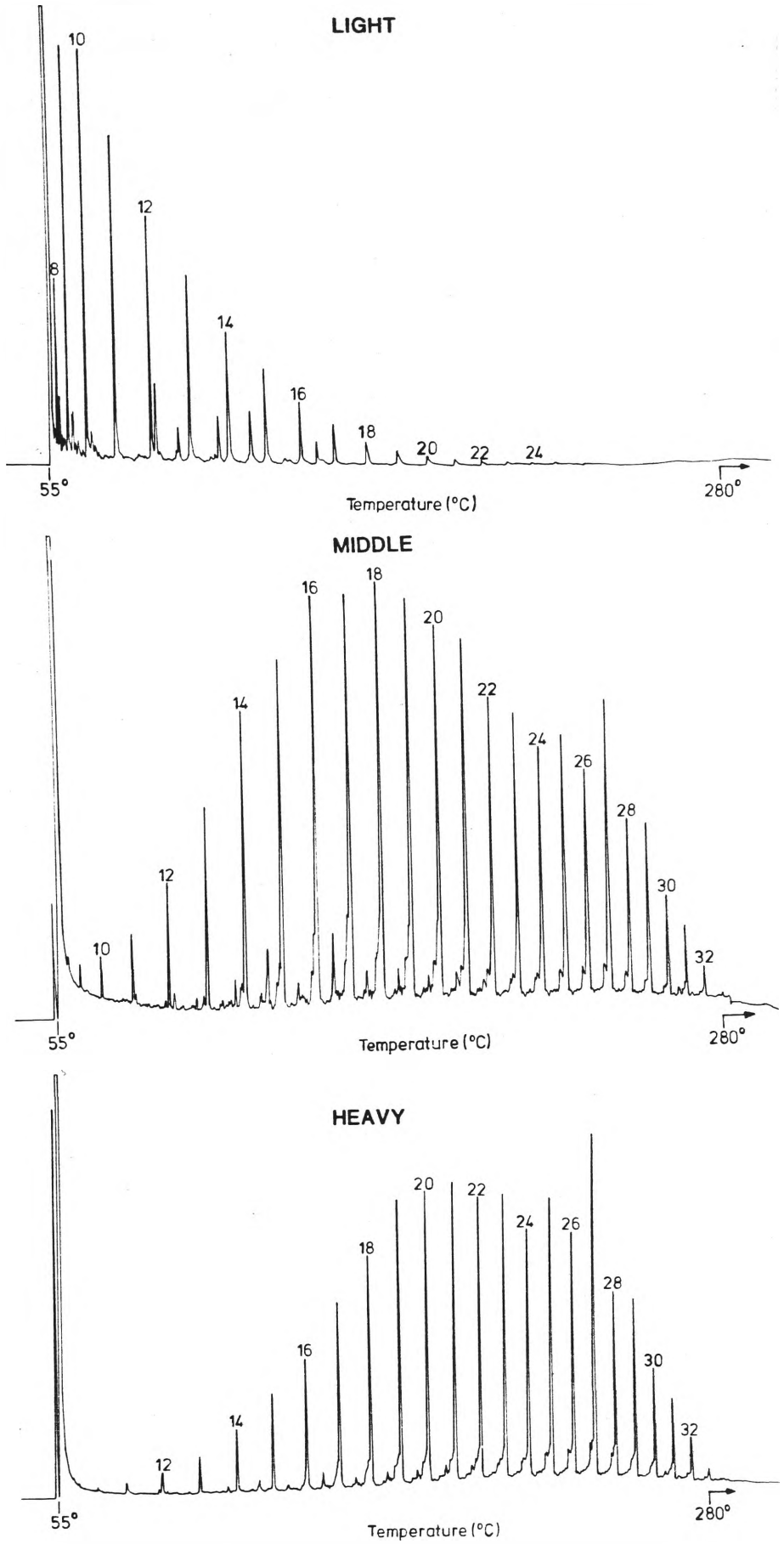


Figure 20. Gas chromatograms of the total alkane fractions from the Lurgi light, middle and heavy oils. Carbon numbers of homologous linear alkanes are indicated.

and alkyl-cyclopentanes (C_5 - C_{11} alkyl chain) also occur in this fraction. The middle oil contained 3% branched/cyclic alkanes and comprise isoprenoid alkanes (C_{13} - C_{16} and C_{18} - C_{20}), 2- and 3-methyl alkanes (C_{11} - C_{28}), alkylcyclohexanes (C_5 - C_{21} alkyl chain) and alkylcyclopentanes (C_6 - C_{22} alkyl chain) (Figure 21). The dominant compounds in this fraction are the C_{16} and C_{18} isoprenoid alkanes. In the heavy oil the isoprenoid alkanes comprise only a small proportion of the branched/cyclic alkanes. The heavy oil contained 4% of the branched/cyclic alkanes and comprised mainly of 2- and 3-methylalkanes (C_{14} - C_{29}) alkylcyclohexanes (C_7 - C_{22} alkyl chain) and alkylcyclopentanes (C_8 - C_{23} alkyl chain) (Figure 21). The range and type of compounds in the branched/cyclic alkanes of the Lurgi oils is the same as for the Fischer Assay oils. Since the light oil constitutes 67% of the total Lurgi oil, the isoprenoid alkanes are the predominant branched alkanes in the Lurgi oil. This is similar to the Fischer Assay oils.

Both the middle and heavy oil also contained pentacyclic triterpanes in the range C_{27} - C_{30}. These are labelled 'a' to 'd' in Figure 21. The pentacyclic triterpanes were not detected in the Fischer Assay oils probably because the analysis was performed on the whole oil, in which the triterpanes constitute only a minute portion, whereas the Lurgi oil was divided into three fractions and hence the detection of the triterpanes was made easier. It is most probable that the triterpanes also occur in the Fischer Assay oils.

The pentacyclic triterpane with the 17βH, 21βH-hopane carbon skeleton occurs in living organisms and in ancient shales

which have experienced little thermal stress. The predominant fossil fuel hopane isomers, mainly 17αH, 21βH, do not occur in living systems. They arise by transformation during diagenesis of 17βH, 21βH structures (Ensminger et al., 1974). During these transformations the generation of 17βH, 21αH-moretanes is also observed. Pentacyclic triterpanes have been used as maturity indicators for sediments especially (1) the ratio of 17βH-trisnorhopane/17αH-trisnorhopane and (2) the ratio of 17βH, 21αH-30-normoretane/17αH, 21βH-norhopane. These ratios decrease as maturation increases (Seifert and Moldowan, 1978 and 1980).

The dominant triterpane in the middle and heavy oil is the C_{27} 17βH-trisnorhopane. The C_{27} 17αH-trisnorhopane occurs in trace amounts. The second most abundant triterpane is the C_{29} 17αH, 21βH-norhopane followed by the C_{29} 17βH, 21αH-30-normoretane and then the C_{30} 17αH, 21βH-hopane (see Table 16 for structures). These hopanes have been found in solvent extracts from the Kerosene Creek oil shale from the Rundle deposit (Regtop et al., 1983). In the solvent extract it was found that the thermodynamically unstable 17βH-trisnorhopane was also a dominant triterpane and therefore it seems that this hopane remains unchanged during pyrolysis. This is unusual since one would expect the more stable 17αH-trisnorhopane to be formed from the unstable 17βH-trisnorhopane during pyrolysis. The ratio of C_{29} 17βH, 21αH-normoretane to the 17αH, 21βH-norhopane in the middle and heavy oil is 0.7. This is the opposite of that found in the solvent extract where the ratio is 4. (Regtop et al., 1983).

The α,β configuration is the most stable and the β,β configuration the least stable, with β,α being intermediate. The large concentration of the C_{29} 17βH, 21αH-normoretane in the solvent extract of the Kerosene Creek oil shale (Regtop et al., 1983) may suggest that the 17βH, 21αH-30-normoretane is kinetically trapped in the bitumen of the immature shale. During pyrolysis the energy is sufficient for the conversion of 17βH, 21αH-30-normoretane to 17αH, 21βH-norhopane. This may explain the greater concentration of the C_{29} α,β configuration in the Lurgi oil. A significant observation is the preservation of the C_{27} 17βH-trisnorhopane in the Lurgi oil. It would appear that the C_{29} 17βH, 21αH-normoretane is thermally more labile than the C_{27} 17βH-trisnorhopane. In contrast to the bitumens, the pyrolysis products reflect a very different situation, in that, the starting molecules are chemically bonded to the kerogen polymer. The nature of the kerogen hopane linkage is important to the understanding of this stereochemical difference between kerogen pyrolysates and associated bitumens. The attachment of the hopane moiety to some functional linkage in the kerogen matrix could decelerate the conversion of the C_{27} 17βH-trisnorhopane.

B) Alkenes

Linear alkenes constitute 21% of the light oil (Table 12) with the 1-alkenes predominating and ranging from C_8 to C_{25} with a maximum at C_9 (Figure 22). The isomeric 2- and 3-alkenes are in trace amounts compared with the 1-alkenes. In the middle oil, linear alkenes constitute 15% of the oil (Table 12) with the 1-alkenes predominating and ranging from C_9 to C_{34} with a maximum at C_{16} - C_{17}

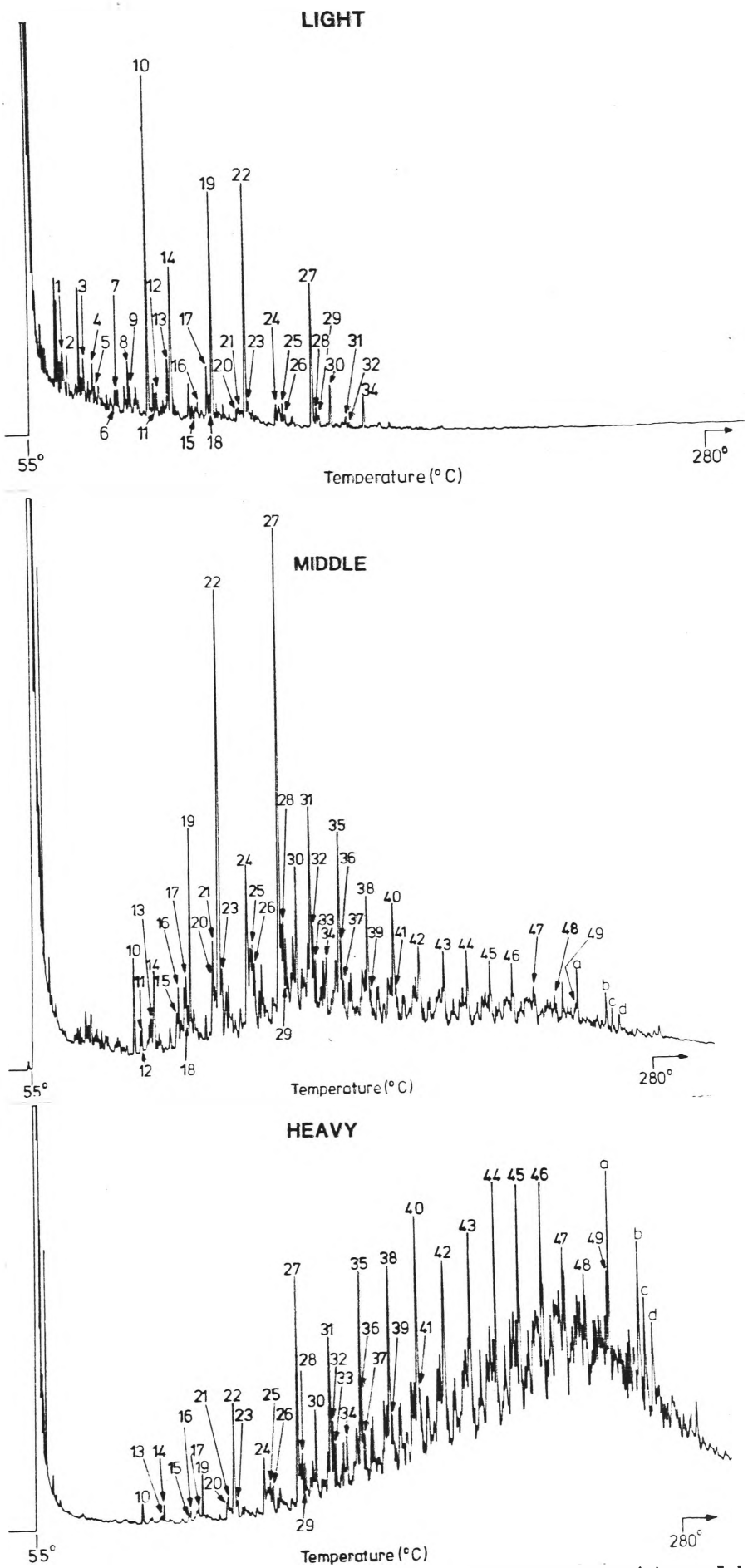


Figure 21. Gas chromatograms of the branched/cyclic alkane fractions from the Lurgi light, middle and heavy oils. Numbers and letters refer to compounds listed in Table 5.

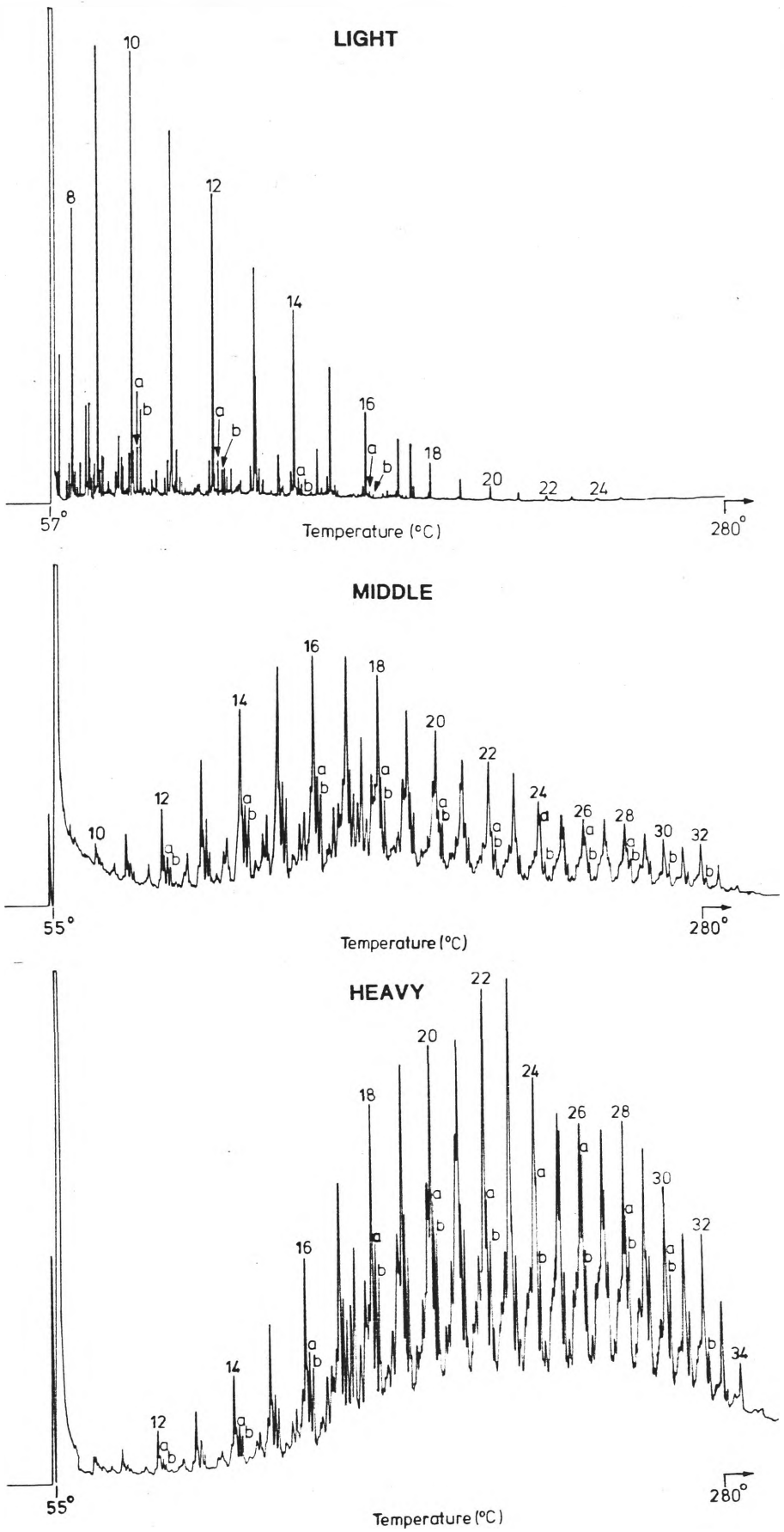


Figure 22. Gas chromatograms of the total alkene fractions from the Lurgi light, middle and heavy oils. Carbon numbers of homologous linear alkenes are indicated. a and b denote homologous 3- and 2-alkenes respectively.

(Figure 22). The ratio of 2- and 3-alkenes to 1-alkenes is similar in both middle and heavy oils. The 3-alkenes also have a bimodal distribution with a maximum at C_{20} and C_{25} (the C_{25} maximum is larger) whereas the 2-alkenes have a maximum at C_{21} and C_{28}.

Since the light oil constitutes 67% of the total Lurgi oil, the bulk of the linear alkenes is mainly 1-alkenes of low molecular weight. Overall, the linear alkenes constitute 19% of the total Lurgi oil as compared with 10% for the Fischer Assay oil from the Kerosene Creek seam. Therefore, the linear alkenes (19%) are in greater concentration than the n-alkanes (11%) in the Lurgi oil. This is in sharp contrast with the Fischer Assay oil from the Kerosene Creek seam where the n-alkanes (23%) are in greater concentration than the linear alkenes (10%).

Figure 23 represents the distribution of the ratio of 1-alkenes/n-alkanes with carbon number for light, middle and heavy oil and for the Fischer Assay oil from Kerosene Creek seam. This shows that the 1-alkenes are in greater concentration that the n-alkanes in the light oil and that the ratio of 1-alkenes/n-alkanes in the light oil decreases as the carbon chain increases. It also shows that in the middle and heavy oil the n-alkanes are in greater concentration than the 1-alkenes but since the total linear alkenes are more abundant than the n-alkanes in the middle and heavy oil (Table 12) this would suggest that there is an increase in isomeric linear alkenes.

It has been reported previously (Burnham et al., 1982) that the rate of heating during pyrolysis affects the ratio of

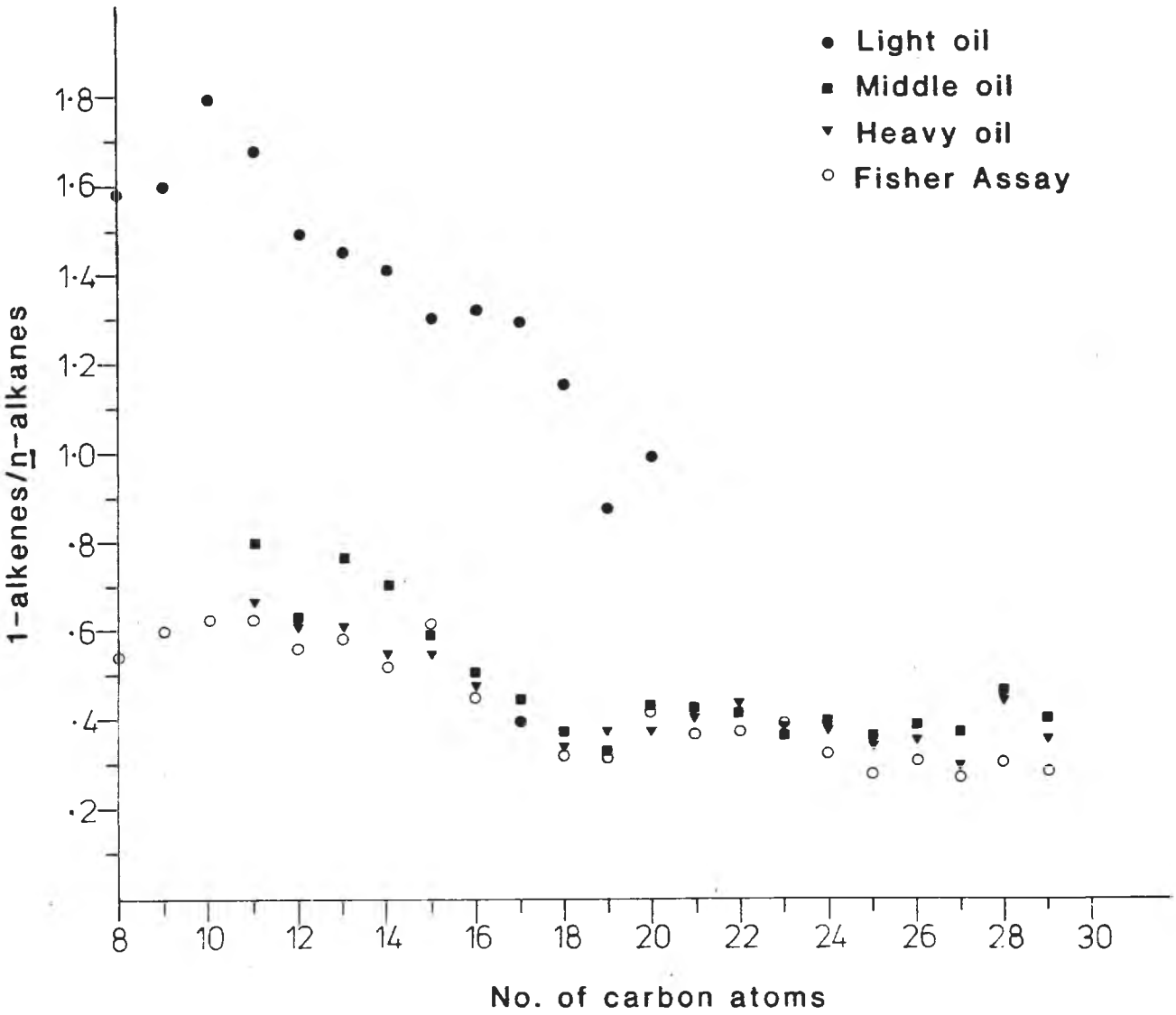


Figure 23. Distribution of the ratio of 1-alkenes/n-alkanes with carbon number for the Lurgi light, middle and heavy oils and for the Fischer Assay oil from the Kerosene Creek seam.

1-alkenes/n-alkanes. This ratio increases as heating rate increases. In the Lurgi process the oil shale is flash pyrolysed up to 500°C within a few seconds, whereas in the Fischer Assay retorting, the oil shale is heated up to 500°C over a period of 40 minutes. The decline in 1-alkene abundance may be due to the greater thermodynamic stability of the 2-, 3- and 4-alkenes. The lower rate of diffusion of the higher molecular weight alkenes would result in longer retention within the mineral matrix. If isomerization is catalysed by mineral surfaces such as silica (Ingram et al., 1983) the higher molecular weight 1-alkenes may experience greater opportunity for positional isomerization.

The composition of branched/cyclic alkenes in the Lurgi oils (Figure 24) was as follows: 1-alkylcyclohexenes with alkyl chain C_4 - C_8 in light oil, C_6 - C_{25} in the middle oil and C_{11} - C_{25} in the heavy oil; alkylcyclopentenes with alkyl chain C_5 - C_{24} in middle oil and C_{12} - C_{26} in the heavy oil; 2-methyl-3-alkenes with linear chain C_9 - C_{14} in the light oil, C_{11} - C_{31} in the middle oil and C_{17} - C_{31} in the heavy oil; 1-methyl-4-alkylcyclohexenes with alkyl chain C_4 - C_7 in the light oil, C_6 - C_{24} in the middle oil and C_{12} - C_{26} in the heavy oil (Table 6). The most abundant compound in the light oil was tentatively identified as 7-methyl-6-tridecene. Only one pristene isomer was detected in the light oil and it was the second most abundant peak.

It is most likely that the double bond in the pristene is in the terminal position. The other pristene isomers are not likely to be formed for the same reason as for the linear alkenes. Three isomers of pristene, identified in the middle

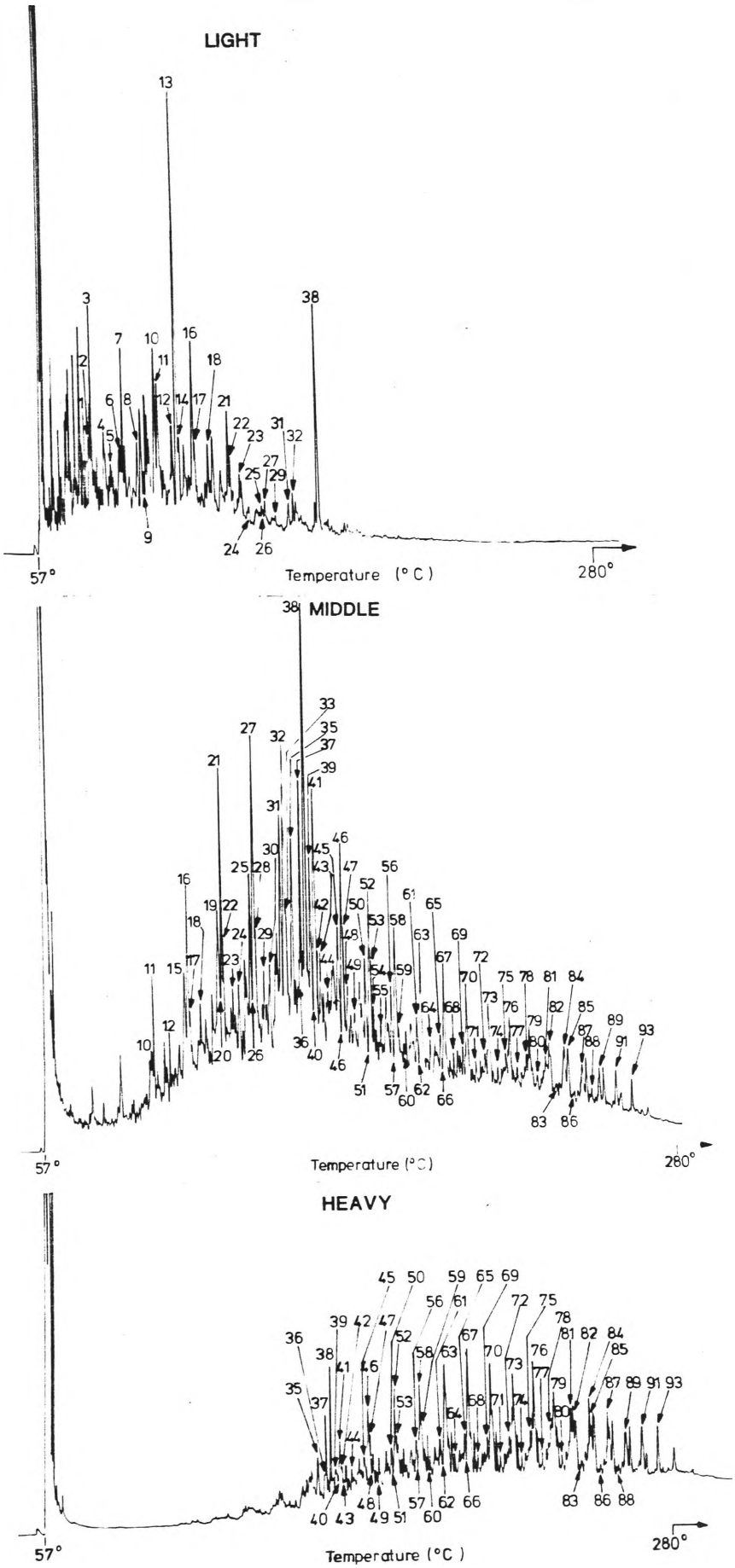


Figure 24. Gas chromatograms of the branched/cyclic alkene/alkylbenzene fractions from the Lurgi light, middle and heavy oils. Numbers refer to compounds listed in Table 6.

and heavy oils, were the most abundant compounds in both of these oils. The branched/cyclic alkene fractions also contained an homologous series of alkylbenzenes which were quite prominent in the middle and heavy oils. Overall, the branched/cyclic alkenes and monosubstituted benzenes constituted 8% of the total Lurgi oil which is similar to the Fischer Assay oils.

C) Aromatics

Homologous series of 1- and 2-phenylalkanes were identified in the branched/cyclic alkene fractions (Figure 24, Table 6). The linear chain lengths were C_4 - C_{11} in the light oil, C_5 - C_{26} in the middle oil and C_{12} - C_{26} in the heavy oil. The diaromatic fraction in the light oil (Figure 25) constituted 15% of the oil and contained polysubstituted benzenes, substituted indans, methyl and dimethylnaphthalenes (Table 7). Polysubstituted benzenes were the most abundant compounds in this oil with 1,2,4- and 1,2,3-trimethylbenzene the dominant compounds (Figure 25). The diaromatic fraction constituted 11% of the middle oil (Table 12) and contained polysubstituted benzenes, substituted indans and homologous series of 1- and 2-alkylnaphthalenes (C_1 - C_{22} alkyl chain), 1-phenyl-4-alkenes (C_{11} - C_{28} linear chain) and 6-alkyl-1,2,3,4-tetrahydronaphthalenes (C_1 - C_{17} alkyl chain) (Figure 25, Table 7). 1- and 2-methylnaphthalene and ethylnaphthalene were the most abundant compounds in the middle oil. The heavy oil contained 11% of the diaromatic fraction and comprised the same type of compounds as in the middle oil. The g.c. profile of the diaromatic fraction in the heavy oil (Figure 25) shows that there is more unresolved high molecular weight material than in the middle oil. Overall, the diaromatic

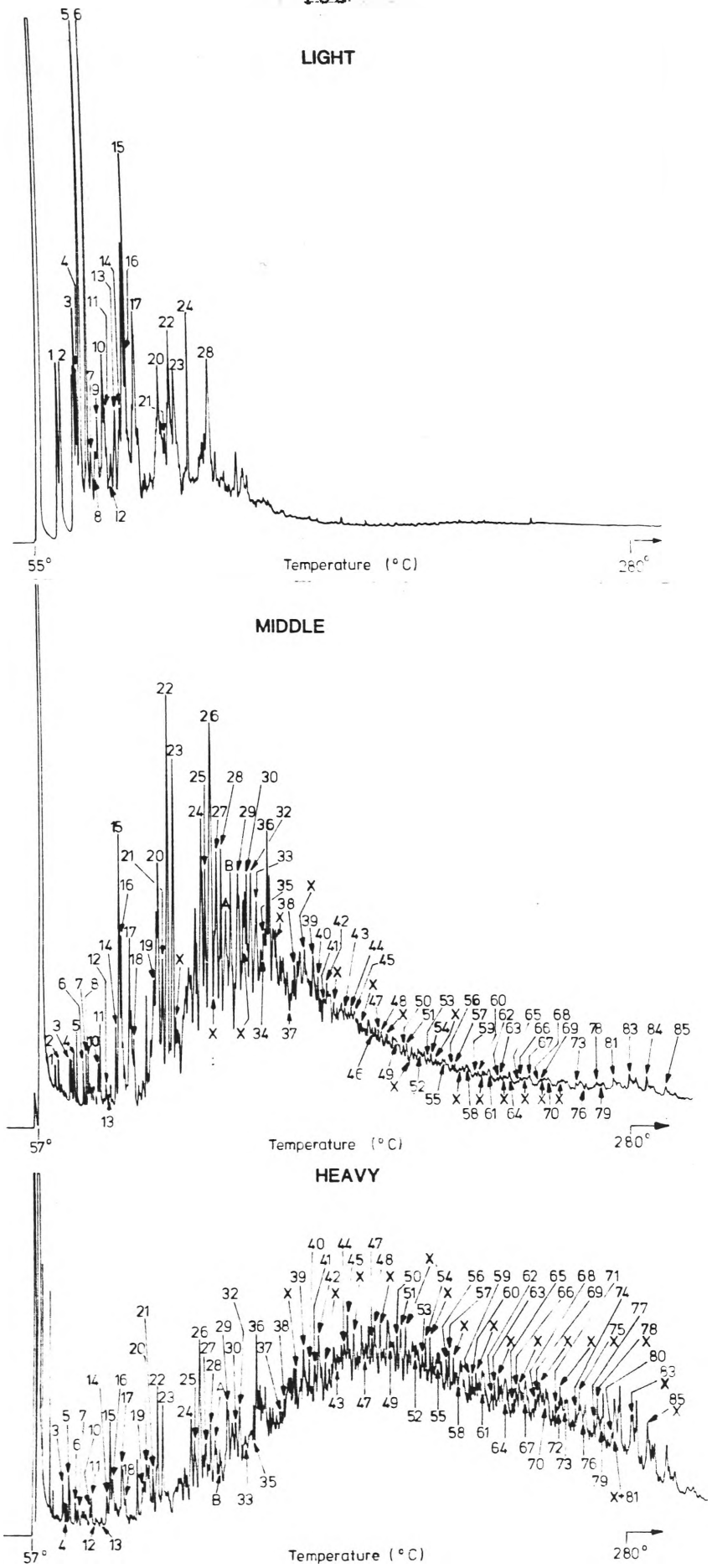


Figure 25. Gas chromatograms of the diaromatic fractions from the Lurgi light, middle and heavy oils. Numbers refer to compounds listed in Table 7. X denotes homologous 6-alkyl-1,2,3,4-tetrahydronaphthalenes. A=1,2-dimethylnaphthalene; B=acenaphthene

fraction constituted 14% of the total Lurgi oil and comprised mainly polysubstituted benzenes.

The polyaromatic hydrocarbon (P.A.H.) fractions in the Lurgi oils (Figure 26) contained aromatic compounds with 3 - 5 rings and their partially hydrogenated derivatives (Table 8) similar to the Fischer Assay oils. The P.A.H. constituted 5% of the light oil and contained mainly fluorene, phenanthrene, fluoranthene and pyrene. Phenanthrene is by far the most abundant compound in the light oil (Figure 26) but anthracene, which is the isomer of phenanthrene, is in trace amounts. The concentration of anthracene, relative to phenanthrene, increased in the middle and heavy oil. The P.A.H. fraction constituted 11% in the middle and heavy oil.
The concentration of aromatic compounds, greater than four rings, increased in the middle and heavy oils as would be expected in high boiling fractions. The ratio of fluoranthene to pyrene, for the light, middle and heavy oil is 2, 1.1 and 0.7 respectively. Since 67% of the Lurgi oil is due to the light oil, it would appear that fluoranthene is formed in preference to pyrene in the Lurgi oil. This is opposite to the Fischer Assay oils where pyrene is formed in preference to fluoranthene (ratio of fluoranthene to pyrene is 0.3).
It appears that the rate of heating may determine the type of polyaromatic hydrocarbons formed. This is important since some polyaromatic hydrocarbons are known to be potential carcinogens and provide a hazard to health and environment.
Overall, the P.A.H. fraction constituted 7% of the total Lurgi oil which is similar to the Fischer Assay oils.

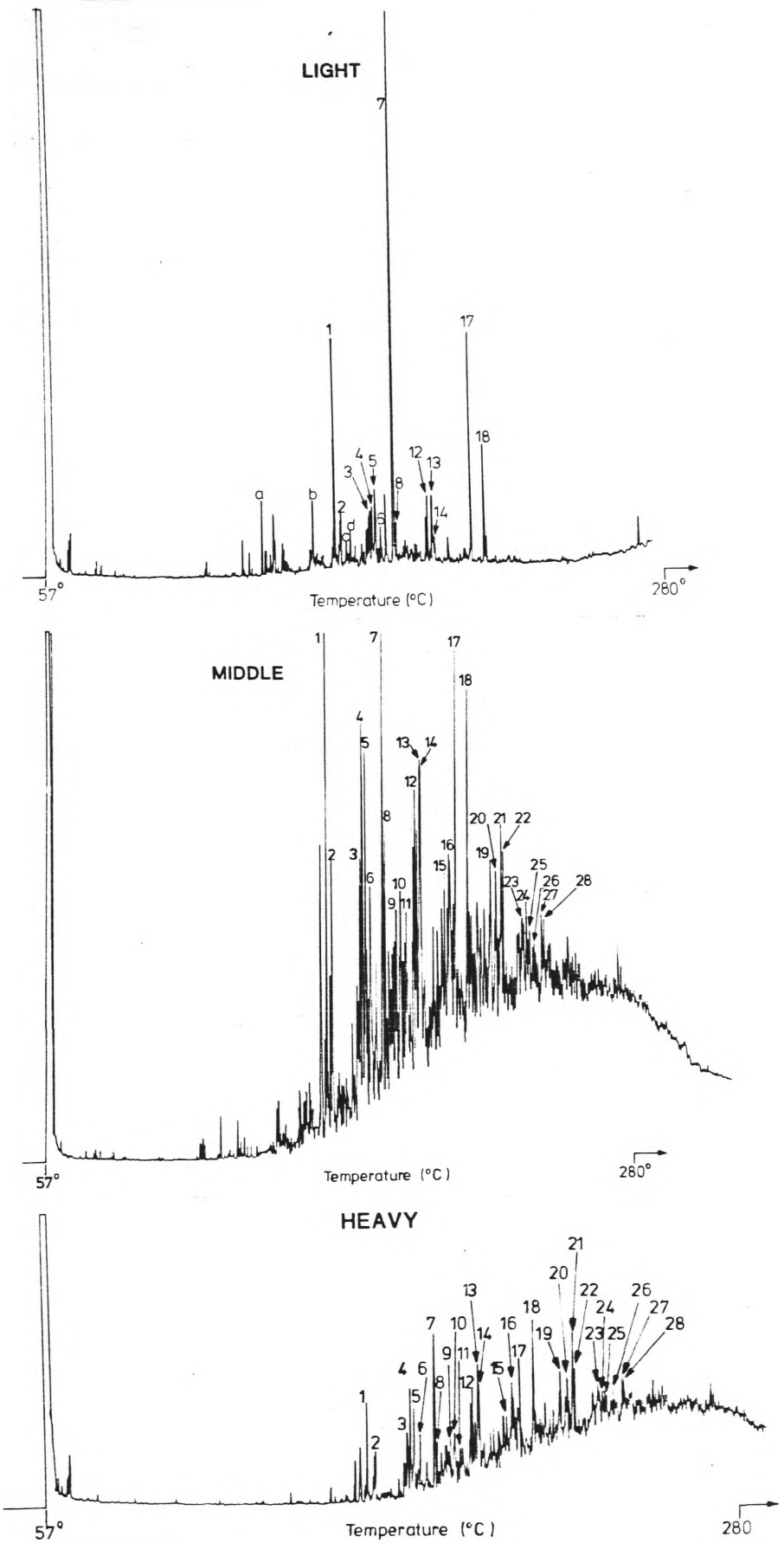


Figure 26. Gas chromatograms of the polyaromatic fractions the Lurgi light, middle and heavy oils. Numbers refer to compounds listed in Table 8. a=acenaphthene or biphenyl; b=dibenzofuran c and d=xanthene and/or 4-phenylbenzaldehyde

D) Nitriles

Saturated aliphatic nitriles occur in the Lurgi oils and range from C_5 - C_{16}, with a maximum at C_9, in the light oil; C_7 - C_{31} with maxima at C_{14}, C_{18} - C_{20} and C_{28}, and even carbon number preference in the region C_{18} - C_{30}, in the middle oil; and C_7 - C_{32} with maxima at C_{19} and C_{28} and even carbon number preference in the region C_{22} - C_{30}, in the heavy oil (Figure 27). The main g.c. peaks are preceded by smaller peaks labelled 'a' whose mass spectral fragmentation patterns are suggestive of unsaturated aliphatic nitriles. The characteristic mass spectral ions for these compounds are m/e 41, 55, 69, 80, 94, 108, 122, 136, M-1. These compounds did not appear in the g.c. profiles of the Fischer Assay oils probably due to the inefficiency of the g.c. column at the time. The nitriles in the Lurgi oil were chromatographed using a vitreous silica capillary column. Aromatic nitriles, namely benzonitrile and o, m, p-tolunitrile, were detected in the light oil (Figure 27; Table 13). No aromatic nitriles were detected in the middle and heavy oils or in the Fischer Assay oils. The nitrile fraction constituted 6%, 5% and 6% of the light, middle and heavy oils respectively (Table 12). Since the light oil constitutes 67% of the total Lurgi oil, the aliphatic nitriles in the Lurgi oil are mainly of low molecular weight. This is different to the Fischer Assay oils where the bulk of the aliphatic nitriles resembles the nitriles in the middle and heavy oils. Overall, the nitrile fraction constituted 6% of the total Lurgi oil similar to the Fischer Assay oil from the Kerosene Creek seam.

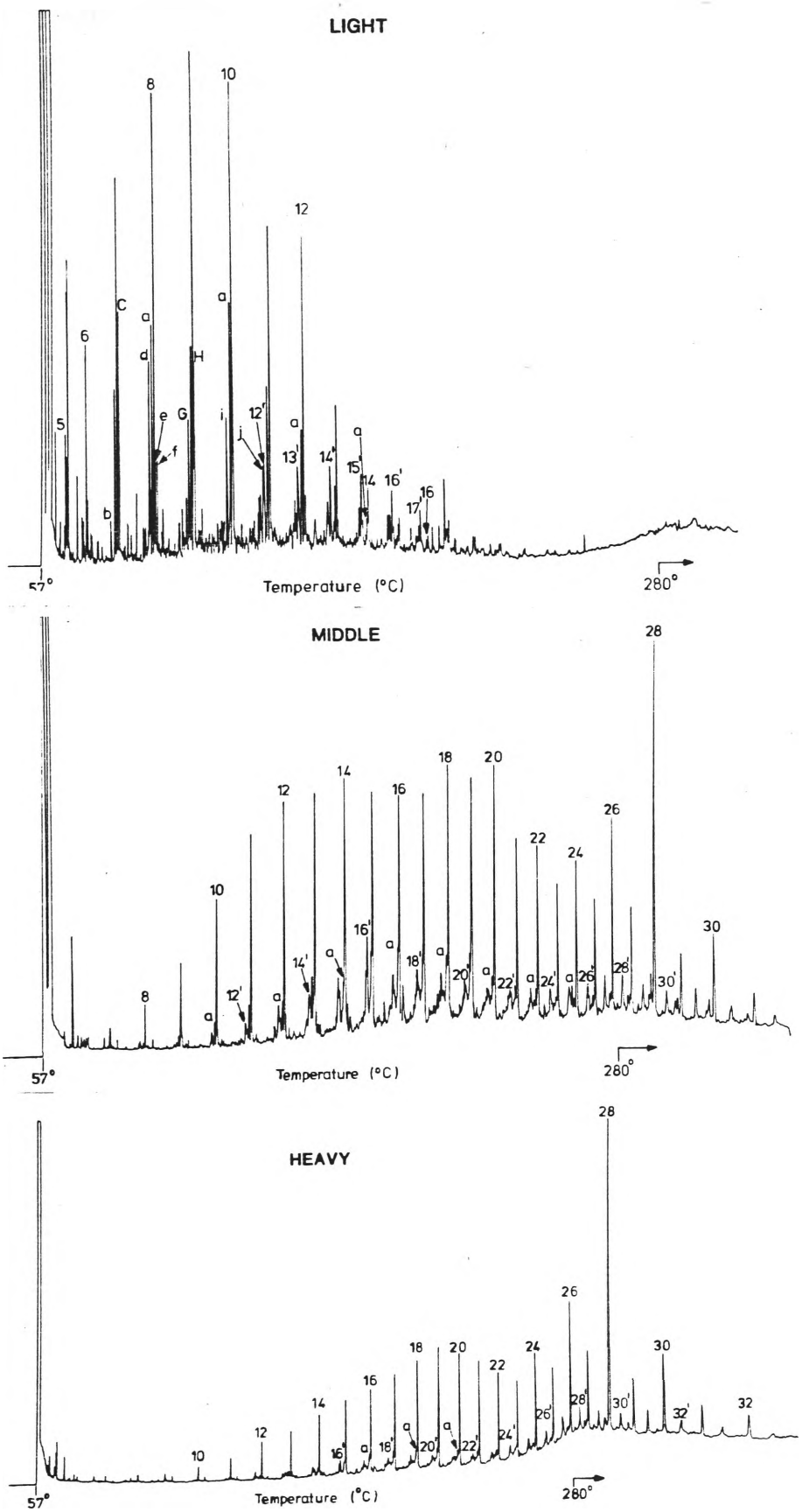


Figure 27. Gas chromatograms of the nitrile fractions from the Lurgi light, middle and heavy oils. Carbon numbers are indicated for homologous saturated straight-chain alkylnitriles (no prime) and 6-alkanones (with prime). a denotes homologous unsaturated alkylnitriles. Letters b to j refer to compounds listed in Table 13.

Table 13. Compounds identified in the nitrile fraction of the Lurgi light oil

Peak[1] No.	Identity
b	benzaldehyde
c	benzonitrile
d	o-tolunitrile
e	m-tolunitrile
f	p-tolunitrile
	3-nonanone
g	propiophenone
h	3-decanone
i	butyrophenone
j	valerophenone

(1). Letters refer to peaks in Figure 27.

E) Ketones

In the nitrile fractions of the light, middle and heavy oils (Figure 27), there is evidence of homologous series of 3-, 4- and 6-alkanones in trace amounts. The 4-alkanones co-eluted with the aliphatic nitriles. The characteristic mass spectral ions for these ketones are as follows:

(1) 3-alkanones, m/e 43, 57, 72 (base peak), 85, M-29;

(2) 4-alkanones, m/e 43, 58, (base peak), 71, 86, M-43;

(3) 6-alkanones, m/e 43, 58, 71, 85, 99, 113, M-71.

The 6-alkanones are indicated by the numbers labelled with a prime (Figure 27). A possible origin of 3-alkanones is the decarboxylation, during pyrolysis, of β-ketoesters of the type $RCOCH(CH_3)COOR$ under neutral or acidic conditions. 2-Alkyl-substituted fatty acids have been observed in certain classes of bacteria (O'Leary, 1970). At this stage, the origin of 4- and 6-alkanones has not been postulated. Also detected in the nitrile fraction of the light oil were the aromatic ketones propiophenone, butyrophenone and valerophenone (Figure 27; Table 13). These are characterised by mass spectral ions of m/e 51, 77, 105 (base peak).

Saturated and possibly unsaturated methyl ketones were detected in the methyl ketone fractions. The saturated methyl ketones ranged from C_6 - C_{17} in the light oil with a possible maximum at C_{10} - C_{11}; C_8 - C_{30} in the middle oil with maxima at C_{13}, C_{17} and C_{19} and odd carbon number preference in the region C_{23} - C_{30}; C_{12} - C_{33} in the heavy oil with maxima at C_{19} and C_{29} and odd carbon number preference in the regions C_{17} - C_{21} and C_{23} - C_{30} (Figure 28). The saturated methyl ketones are the predominant compounds in the methyl ketone

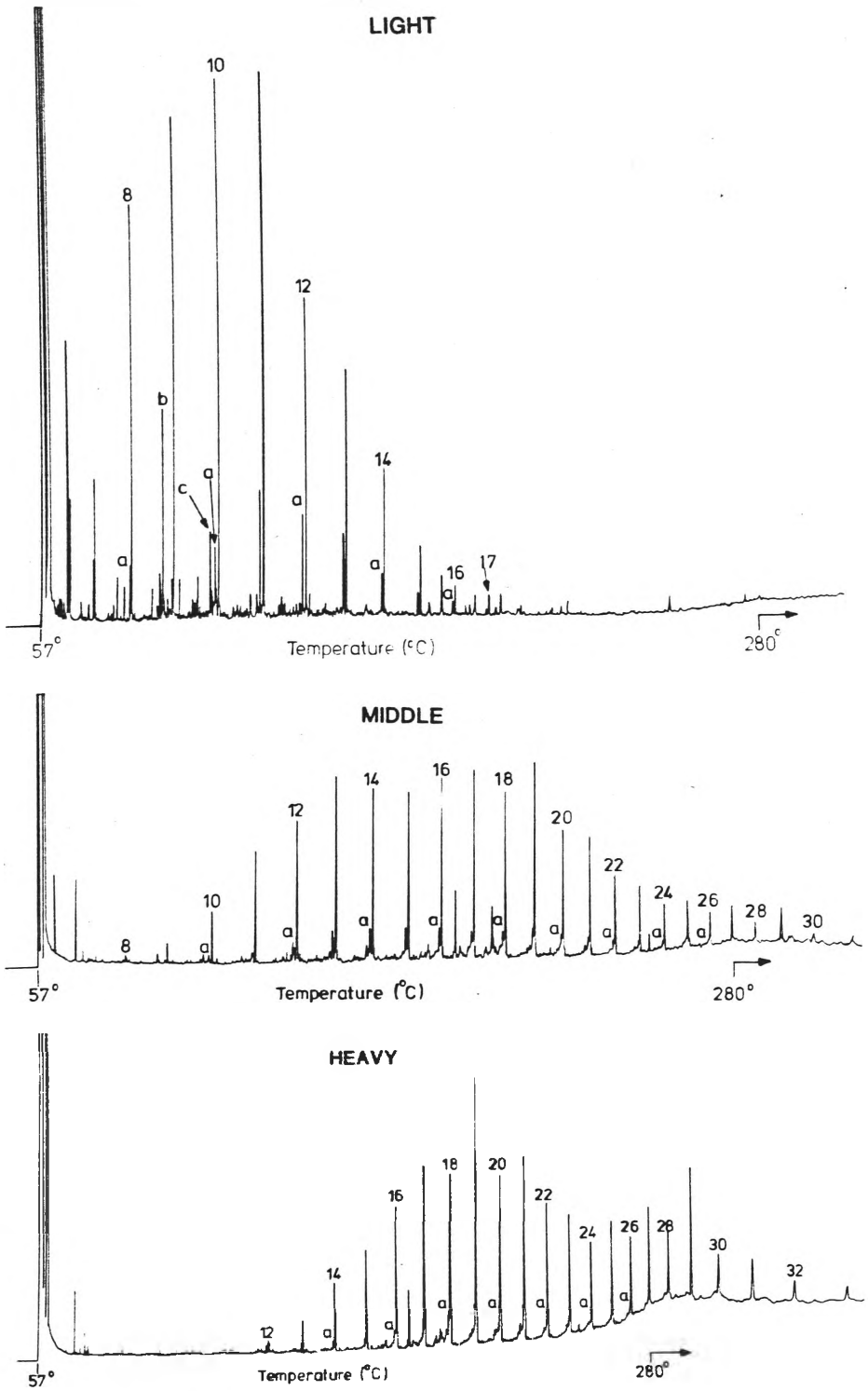


Figure 28. Gas chromatograms of the methyl ketone fractions from the Lurgi light, middle and heavy oils. Carbon numbers of homologous 2-alkanones are indicated. a denotes a series of homologous unsaturated straight-chain methyl ketones. b = acetophenone; c = methylacetophenone

fraction with the unsaturated methyl ketones in trace amounts. The distinct odd carbon number preference is indicative of a biological precursor as suggested previously. Acetophenone and methylacetophenone was also detected in the light oil. The methyl ketone fraction constitutes 5%, 5% and 6% of the light, middle and heavy oils, respectively. Overall, the methyl ketone fraction constitutes 5% of the total Lurgi oil, the bulk of which is low molecular weight methyl ketones since the light oil comprises 67% of the Lurgi oil. This is different to the Fischer Assay oils where the distribution of methyl ketones resembles the middle and heavy Lurgi oils.

F) Methanol fraction

No amides were detected in the Lurgi oil. This differs from the Fischer Assay oils where trace amounts of aliphatic amides were detected. Amides have been detected in the solvent extract of the Kerosene Creek oil shale (Regtop et al., 1983) and therefore amide linkages may be important structural elements in the Rundle kerogen. This would account for the detection of amides in the shale oil but if amides are totally dehydrated to nitriles during the retorting process, this may explain the disappearance of amides in the Lurgi oil.

The methanol fraction from the open column chromatography of the Lurgi oils did not contain amides but saturated and unsaturated aliphatic methyl esters from C_{12} - C_{18}. Also an unknown series with a characteristic mass spectral ion m/e 118 (base peak) was detected in the methanol fraction. Figure 29 represents a typical g.c. profile of these esters. The methyl esters may not be indicative of the shale oil even

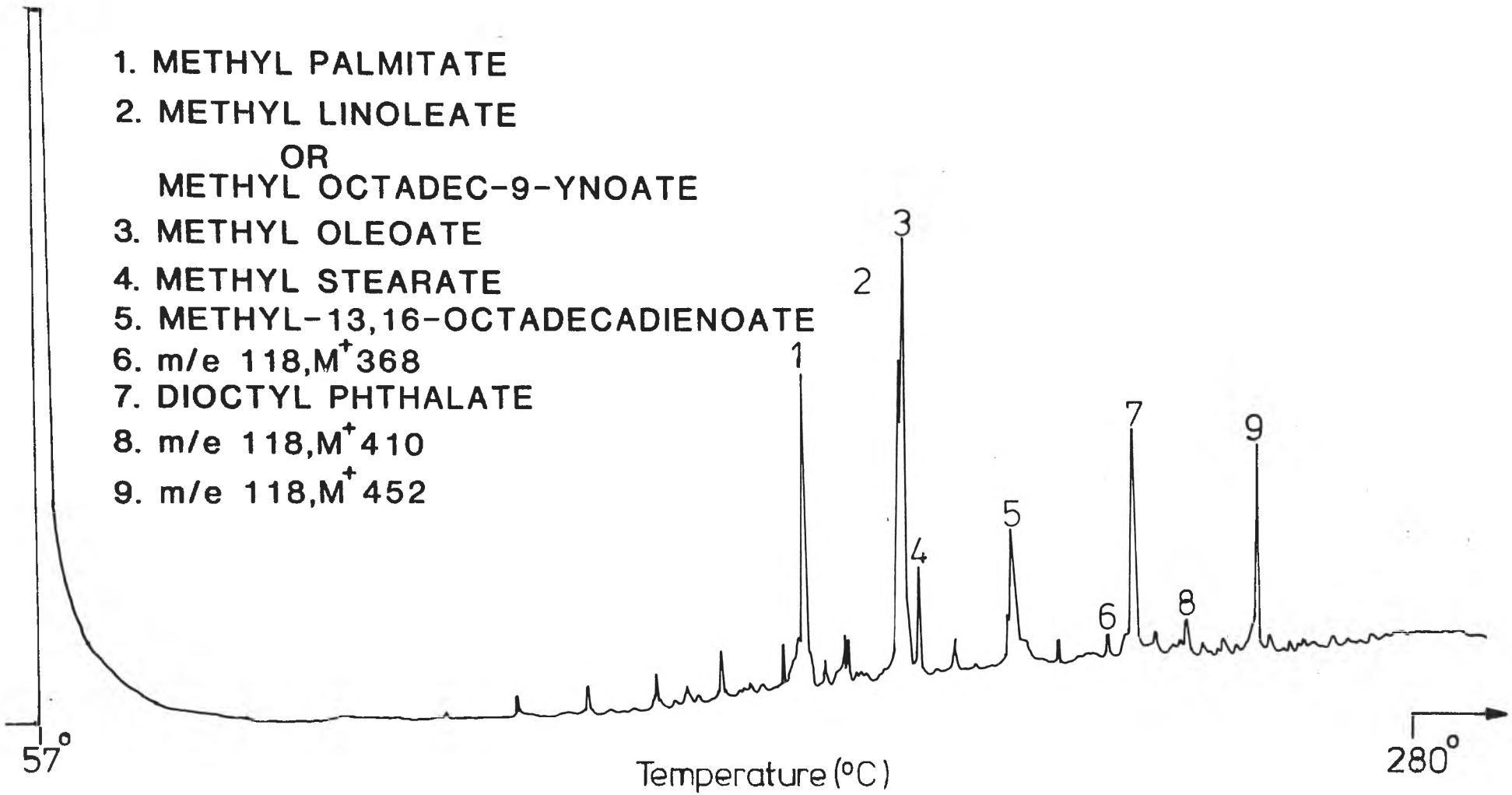


Figure 29. Gas chromatogram of the methyl ester fraction from the Lurgi oils

though ester linkages do occur in kerogen. If there were trace amounts of acids in the methanol fraction, these may be methylated to methyl esters by the methanol in the presence of the silica gel. However, no methyl esters were detected in the Fischer Assay oils. The methanol fraction also contains polymeric material.

G) Acidic and basic compounds

The acidic fraction constituted 1%, 2% and 0.8% of the light, middle and heavy oils respectively. The light oil contained phenol and substituted phenols with phenol, o and m-cresol and 2,4-dimethylphenol being the dominant compounds (Figure 30; Table 14). Naphthols were not detected in the light oil but their abundance increased in the middle and heavy oils relative to the phenols (Figure 30). Since the light oil fraction represents 67% of the Lurgi oil, the bulk of the acidic fraction is substituted phenols similar to those found in the Fischer Assay oils. The acidic fraction of the Lurgi oils was analysed on a vitreous silica g.c. capillary column whereas a glass capillary column was used for the Fischer Assay oil. The vitreous silica capillary column produced better resolution (Figures 17 and 30).

The light, middle and heavy oils contained 6%, 3% and 2%, respectively, of basic compounds. The light oil contained predominantly substituted pyridines and smaller amounts of quinolines and tetrahydroquinolines. The middle oil contained mostly substituted quinolines and trace amounts of acridines, whereas the heavy oil contained acridines and smaller amounts of quinolines (Figure 31). The g.c. profiles show that there is a large proportion of unresolved material, especially in the middle and heavy oil, due to high molecular weight

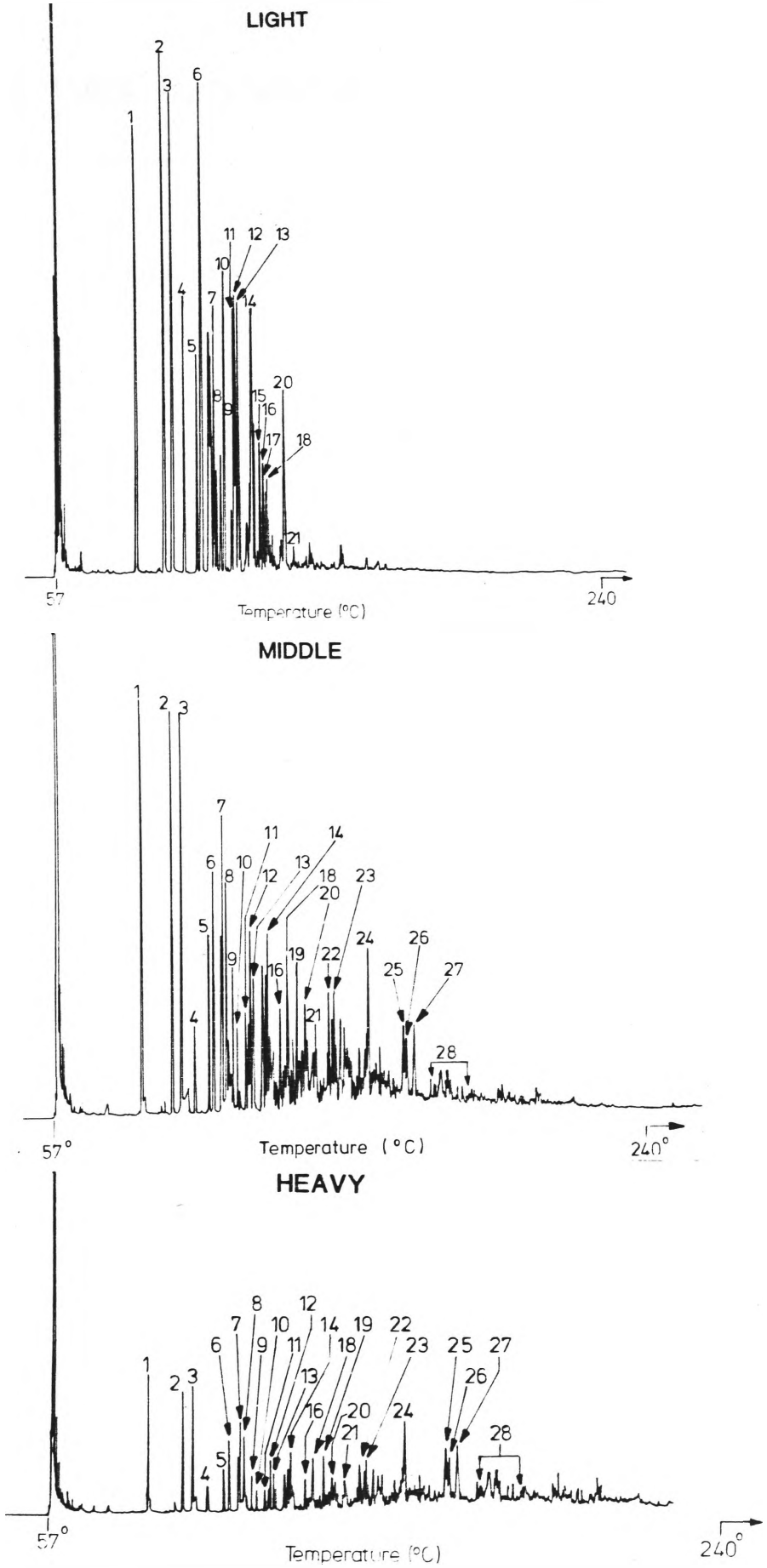


Figure 30. Gas chromatograms of the phenolic (acidic) fractions from the Lurgi light, middle and heavy oils. Numbers refer to compounds listed in Table 14.

Table 14. Phenolic compounds identified in the Lurgi oils

Peak No.(1)	Identity
1	phenol
2	o-cresol
3	m-cresol
4	2,6-dimethylphenol
5	dimethylphenol
6	2,4 or 2,5-dimethylphenol
7	2,3-dimethylphenol
8	dimethylphenol
9	3,4-dimethylphenol
10	2,4,6-trimethylphenol
11	2,3,6-trimethylphenol
12	trimethylphenol
13	3-ethyl-5-methylphenol
14	2,3,5-trimethylphenol
15	diethylphenol
16	sec-and/or tert-butylphenol isomers
17	
18	
19	
20	methylallylphenol
21	
22	amylphenol
23	m/e 148, 147
24	1-naphthol
25	methyl-1-naphthol isomers
26	
27	
28	dimethyl-1-naphthol isomers trimethyl-1-naphthol isomers

(1) Numbers refer to peaks in Figure 30

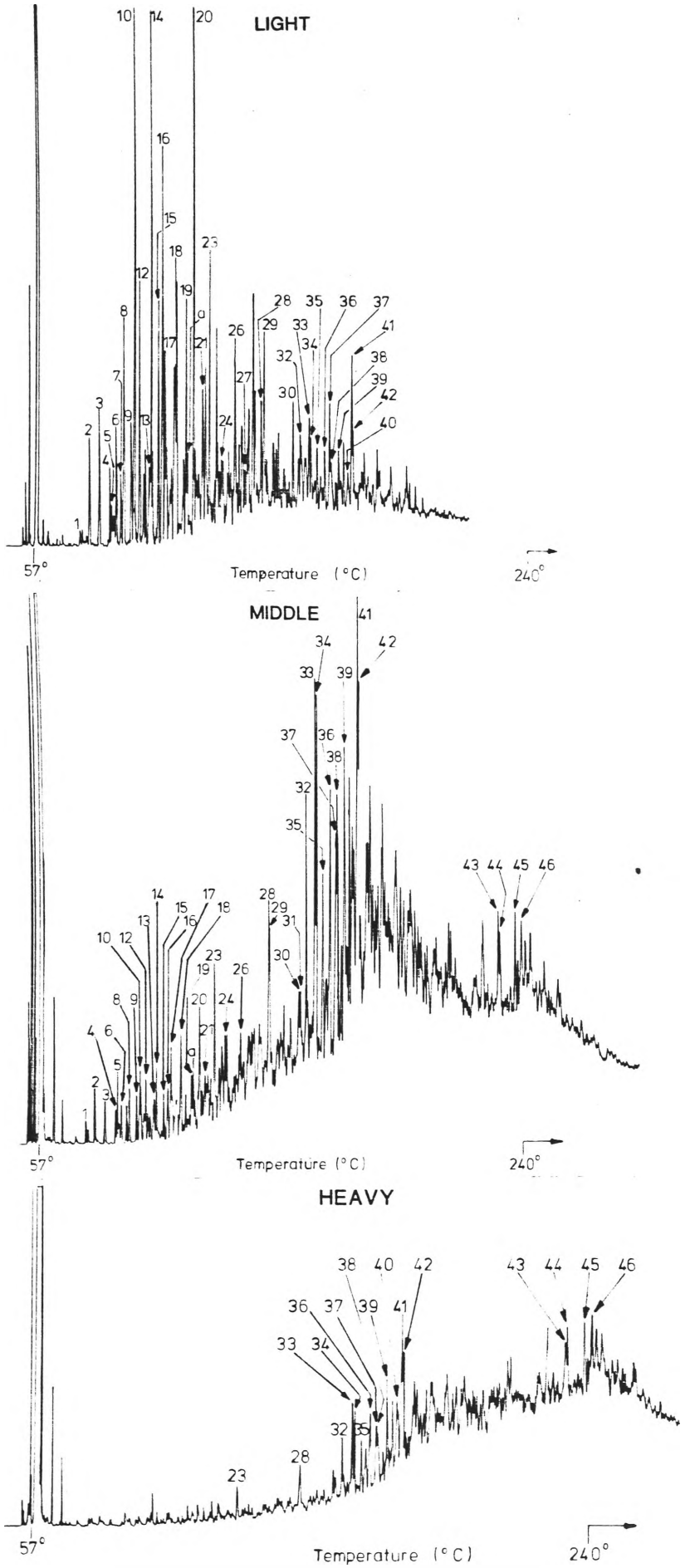


Figure 31. Gas chromatograms of the basic fractions from the Lurgi light, middle and heavy oils. Numbers refer to compounds listed in Table 10.

compounds. Overall, the basic compounds constitute 5% of the total Lurgi oil and consist mainly of substituted pyridines similar to those found in the Fischer Assay oils.

H) Polymeric material

The amount of tar (polymeric material) fraction resulting from acidic and basic extractions was 1.5%, 3% and 3% for the light, middle and heavy oil respectively. Overall, the amount of tar was 2% of the total Lurgi oil. This compares with 11% for the Fischer Assay oil from the Kerosene Creek seam. The polymerization, due to the acidic and basic extractions, may depend on the age and composition of the oil. The neutral fractions also contained brown polymeric material which eluted with chloroform from the open chromatographic column. This polymeric material constituted 8%, 16% and 16% of the light, middle and heavy oils respectively. This shows that the polymeric material arises mainly from the polymerization of high molecular weight compounds since the middle and heavy oil contained the greatest amount of the polymerized material. This is also evident in the formation of asphaltenes which are polymers of high molecular weight. The amount of asphaltene in the light, middle and heavy oils is 0.8%, 3% and 6%, respectively.

3. Extractable components of oil shale

In order to understand the pyrolytic origins of the constituents of retort oil, it is necessary to study the original organic material in the oil shale. Therefore, oil shale from the Kerosene Creek seam (13.2% total organic carbon (TOC)) and a carbonised oil shale (0.7% TOC) were chosen to examine the solvent extractable components and the kerogen degradation products. By studying the solvent extractable components of these two shales and their kerogen degradation products, inferences may be drawn concerning the maturation and origin of the kerogen. Unfortunately, the carbonised oil shale has experienced so much heat that many molecular markers have disappeared.

From an oil shale, studies of retort oils and solvent extracts are complementary. Retort oil provides a gross indication of the constitution of the parent kerogen but the high temperature used for pyrolysis (ca $500^{o}C$) induces many structural rearrangements and creates a wider range of functional groups than was originally present in the parent kerogen. Solvent extracts are obtained under more gentle thermal conditions ($\leq 100^{o}C$) which produce fewer chemical rearrangements and it has been shown, (Gallegos, 1971, 1973; Regtop et al., 1983) that solvent extracts are much richer than retort oils in molecular markers (e.g. steroids and triterpenoids) from which inferences may be drawn concerning the origin and history of the kerogen. Molecular markers

have been used previously in studies of petroleum formation (Philp et al., 1981), biodegradation (Seifert and Moldowan, 1979), oil-oil and oil-source rock correlation (Seifert and Moldowan, 1978; Pym et al., 1975). Their use depends on their moderate to high geological stability and the limited number of structural possibilities of their biogenic precursor molecules. During maturation they are systematically altered through thermocatalytic and microbial processes to give a mixture of new, but structurally similar, molecules. Thus molecular markers indicate the thermal history of the organic matter, the extent to which it has been modified by microbial action and the types of organic input. They do not, however, establish the relative proportions of different source materials because a solvent extract contains only a small proportion of the total organic matter in the oil shale and therefore may not be representative of the shale as a whole. The solvent extract from the Kerosene Creek and the carbonised oil shale constitutes 7 and 16% of the total organic carbon respectively.

The retort oil from the Rundle deposit has already been discussed previously in this thesis and it is the purpose here to provide complementary data on the composition of solvent extracts of the oil shale. In order to probe a larger proportion of the organic matter than is available by solvent extraction, either direct methods, such as infrared spectroscopy (Rouxhet and Robin, 1978) and "magic angle" n.m.r. (Resing et al., 1978) or else chemical degradation procedures are

Table 15. Gravimetric results for the Kerosene Creek and carbonised oil shale

	Percentage mass	
	Kerosene Creek oil shale	Carbonised oil shale
% total organic carbon (TOC)	13.2	0.7
Solvent extract (% of TOC)	7.0	16.0
Acids recovered by alkaline hydrolysis (% of TOC)	2.0	2.0
Acids recovered by permanganate oxidation (% of TOC)	58.0	30.0
Fraction	**Percentage mass of extractable organic matter (% of EOM)**	
Total alkane/alkene	2.1	-
Total alkane + elemental sulphur	-	11.8
Branched/cyclic alkane/alkene	1.0	-
Mono- and diaromatic	1.1	3.3
Polyaromatic	8.1	3.8
Porphyrin and aliphatic, steroidal, triterpenoid alcohol	1.9	-
Porphyrin and ketones	-	1.8
Amide	2.2	6.2
Carboxylic acid	9.7	7.4
Polymeric	8.7	13.3
Asphaltene	66.2	52.2

employed. The results of alkaline hydrolysis and stepwise permanganate oxidation of the oil shales are reported in this section of the thesis. Alkaline hydrolysis should release kerogen components which are bound by ester and amide linkages while permanganate is able to oxidise many functional groups and can even cleave labile carbon-carbon bonds (March, 1968).

The open column chomatographic procedure used for separating the Soxhlet extract of the oil shales into various components was similar to that used for the retort oil. In the Soxhlet extract, however, the retention times for the long straight chain alkanes ($\geq C_{27}$) were greater than for the retort oils. As a result, relatively small amounts of n-alkanes greater than C_{27} were detected in the dichloromethane fraction (PAH fraction) but these were separated by re-chromatography on alumina. It is possible that a small amount of asphaltene remained dissolved in solution, even though the asphaltenes were precipitated and separated from the extract prior to chromatography. This dissolved polymeric material may be responsible for the retention of the long chain alkanes.

A) Solvent extractable compounds

(i) Alkanes and alkenes

The n-alkanes detected by the chromatographic procedure in the Kerosene Creek shale ranged from C_{10} to C_{33} with a maximum abundance occuring at C_{31} and a local maximum at C_{14} - C_{16}, whereas the n-alkanes in the carbonised shale ranged from C_{10} to C_{24} with a maximum at C_{14} (Figure 32). The bulk of the n-alkanes, in the Kerosene Creek shale, lying in the region C_{23} - C_{31} and exhibiting strong odd carbon number preference, are typical of terrestrial plant waxes

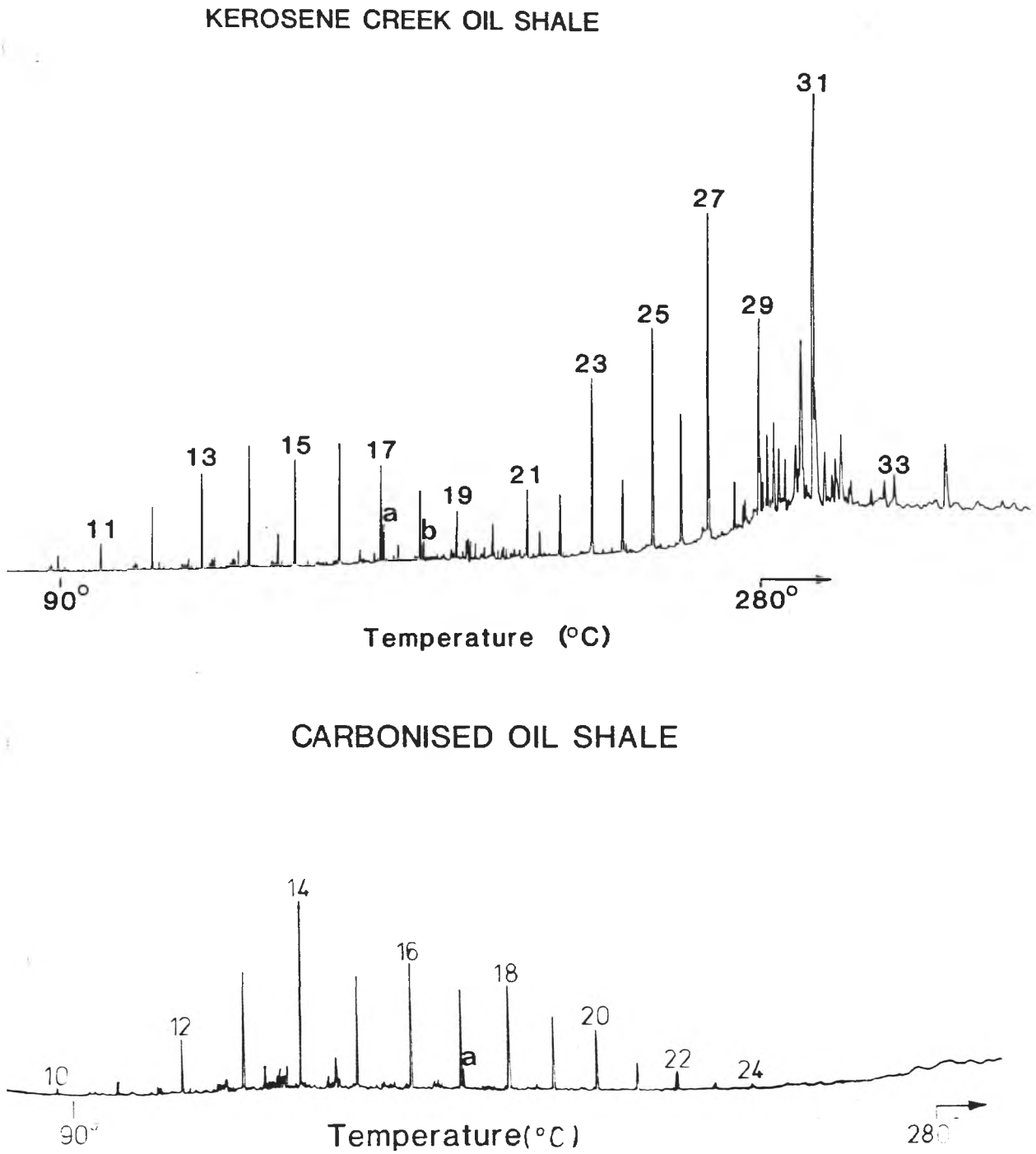


Figure 32. Gas chromatograms of the total alkane/alkene and total alkane fractions from the solvent extracts of the Kerosene Creek and carbonised oil shales respectively. Carbon numbers of homologous straight chain alkanes are indicated. a=pristane; b=phytane

(Eglinton and Hamilton, 1963; Simoneit, 1978). The n-alkanes (Kerosene Creek shale) in the region C_{10} - C_{20} are probably derived from a mixture of algal and bacterial sources; the latter may predominate due to the absence of significant carbon number preference (Oro et al., 1967; Han and Calvin, 1969; Simoneit, 1978). Although petrology indicates that the bulk of the organic matter in the Kerosene Creek oil shale is of algal origin (Hutton, 1983), it appears that terrigenous n-alkanes may be disproportionately represented in the solvent extractable fraction of the organic matter (approx. 1% of the total). The n-alkanes in the Kerosene Creek shale account for 50% of the mass of the total alkanes which in turn represent 2% of the extractable organic matter (Table 15).

The carbonised oil shale does not contain n-alkanes greater than C_{24} (Figure 32). This is due to the thermal cracking of carbon-carbon bonds in long chain n-alkanes to produce shorter chain n-alkanes on exposure to heat from the igneous intrusion. The effects of igneous intrusions have been observed in Jurassic shales, Germany (Leythaeuser et al., 1980). The total alkane fraction constituted 11% of the extractable organic matter, but the majority of this amount was due to the presence of elemental sulphur (S_8) which crystallized when the solvent was evaporated and hence could not be separated from the alkanes. Elemental sulphur may arise from sulphur-producing microorganisms or it may have condensed in the shale as a result of sulphur migrating from the igneous intrusion. No elemental sulphur was detected in the solvent extractable material of the Kerosene Creek oil shale.

The branched/cyclic alkane/alkene fraction in the Kerosene Creek shale consists of acyclic isoprenoid alkanes (C_{13} - C_{20}), steroidal hydrocarbons (C_{27} - C_{30}) and pentacyclic triterpanes (C_{27}- C_{32}) (Table 16), whereas the carbonised shale contains substituted alkylcyclohexanes (C_6 - C_{14} alkyl chain), 2- and 3-methylalkanes (C_{12} - C_{19}) and small amounts of acyclic isoprenoid alkanes (Figure 33, Table 17). The acyclic isoprenoid alkanes C_{13} - C_{20} may arise from diagenetic alteration of the phytol moiety of chlorophyll (Bendoraitis et al., 1962; Cox et al., 1972; Maxwell et al. 1973; Ikan et al., 1975a), from carotenoids (Gallegos, 1976) or, in the case of pristane, also from some genera of zooplankton (Blumer et al., 1964). The high pristane/phytane ratio (1.5) and the presence of significant amounts of C_{13} - C_{20} isoprenoid compounds in the Kerosene Creek oil shale, suggests that some oxidative degradation of phytol occurred during sedimentation and the early stages of diagenesis (Didyk et al., 1978). The ratios of pristane/$\underline{n}$-C_{17} and phytane/$\underline{n}$-C_{18} have been used as maturation indicators in sediments. These ratios decrease as maturation increases. The ratios of pristane/$\underline{n}$-C_{17} and phytane/$\underline{n}$-C_{18} decrease from 0.4 and 0.3 respectively in the Kerosene Creek oil shale to 0.2 and less than 0.05 respectively in the carbonised oil shale (Figure 32). This is due to the thermal cracking of the isoprenoid alkanes resulting in greater quantities of iso (2-methyl) and anteiso (3-methyl) alkanes in the carbonised oil shale (Figure 33).

Squalene was detected in the carbonised oil shale (in the PAH fraction, Figure 36) but was absent in the Kerosene

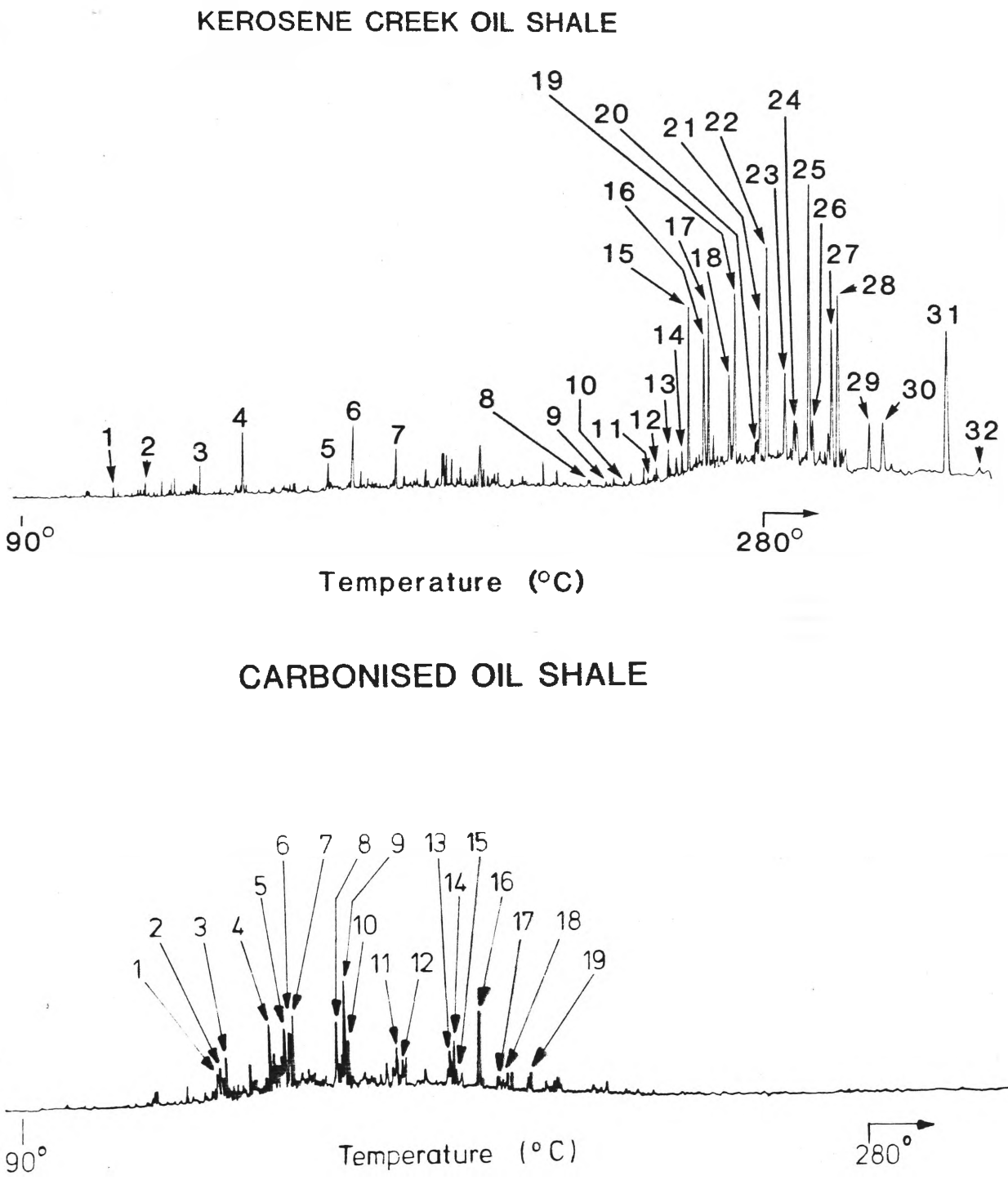


Figure 33. Gas chromatograms of the branched/cyclic alkane/alkene and branched/cyclic alkane fractions from the solvent extracts of the Kerosene Creek and carbonised oil shales. Numbers in the gas chromatograms of the Kerosene Creek and carbonised oil shales refer to compounds in Table 16 and 17 respectively.

Table 16. Branched/cyclic alkanes and alkenes identified in the solvent extract from the Kerosene Creek oil shale

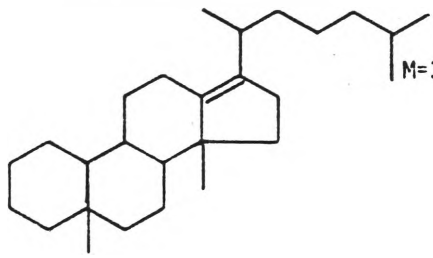
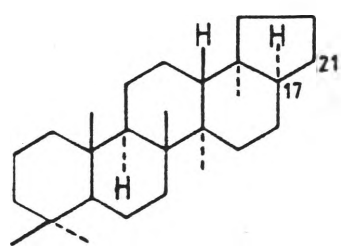
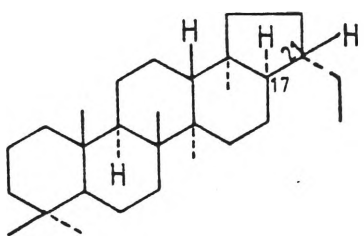
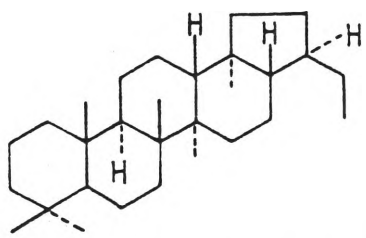
Peak No.[1]	Identify	Characteristic Ions[2]	Reference
1	2,6-dimethylundecane	M=184	
2	2,6-dimethyldodecane	M=198	
3	2,6,10-trimethyldodecane	M=212 113,99,85,71,57*	Stenhagen *et al.*, 1974
4	2,6,10-trimethyltridecane	M=226	
5	2,6,10-trimethylpentadecane	M=254	
6	pristane	M=268	
7	phytane	M=282	
8	$C_{23}H_{38}$	M=314,299,97,45,85,57*	
9	$C_{24}H_{40}$ C_nH_{2n-8} series	M=328,313,285,97,85,57*	Anders & Robinson, 1971
10	$C_{24}H_{40}$	M=328,313,97,85,57*	
11	$C_{25}H_{42}$	M=342,327,191*	
12	20R or 20S-diacholestene 	M=370,355,257*	Rubinstein *et al.*, 1975
13	pentacyclic triterpane $C_{25}H_{44}$	M=356,341,191*	Anders & Robinson, 1971
14	20R or 20S-diacholestene	M=370,355,257*	
15#	20R or 20S-4-methyl-diacholestene	M=384,369,271*	
16	20R or 20S-24-ethyl-diacholestene	M=398,383,257*	Rubinstein *et al.*, 1975
17#	20R or 20S-4-methyl-diacholestene	M=384,269,271*	
18	20R or 20S-24-ethyl-diacholestene	M=398,383,257*	
19#	20R or 20S-24-ethyl-4-methyldiacholestene	M=412,397,271*	
20	17αH-trisnorhopane $C_{27}H_{46}$ 	M=370,149,191* (191/149 = 1.8)	Kimble *et al.*, 1974(a)(b); Wardroper *et al.*, 1977; Seifert & Moldowan, 1980; Jones *et al.*, 1982

Table 16. continued

21#	20R or 20S-24-ethyl-4-methyldiacholestene	M=412,397,271*	Rubinstein *et al.*, 1975
22	17βH-trisnorhopane $C_{27}H_{46}$	M=370,191,149* **(149/191 = 1.3)**	Kimble *et al.*, 1974(a)(b); Wardroper *et al.*, 1977; Seifert & Moldowan, 1980; Jones *et al.*, 1982
23#	20R or 20S-24-ethyl-4-methyldiacholestene *(additional double bond on side chain)*	M=410,395,257*	
24	hopene compound $C_{30}H_{50}$	M=410,395,367,191*	
25	hopene compound $C_{30}H_{50}$	M=410,395,367,231, 191,189,161,136,135	
26	17αH,21βH-norhopane $C_{29}H_{50}$	M=398,191*,177 **(191/177 = 1.2)**	Kimble *et al.*, 1974(a)(b); Wardroper *et al.*, 1977; Seifert & Moldowan, 1980; Jones *et al.*, 1982



27	hopene compound $C_{30}H_{50}$	M=410,395,191*	
28	17βH,21αH-30-normoretane $C_{29}H_{50}$	M=398,191,177* **(177/191 = 1.7)**	Kimble *et al.*, 1974(a)(b); Wardroper *et al.*, 1977; Seifert & Moldowan, 1980



29	17αH,21βH homohopane $C_{31}H_{54}$	M=426,205,191* **(191/205 = 2.9)**	Kimble *et al.*, 1974(a)(b); Wardroper *et al.*, 1977; Seifert & Moldowan, 1980 Jones *et al.*, 1982.

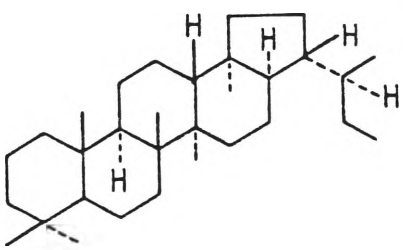
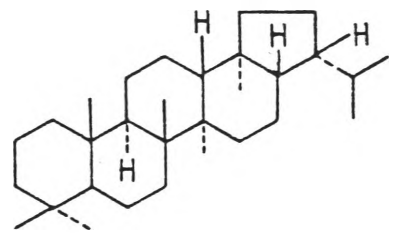
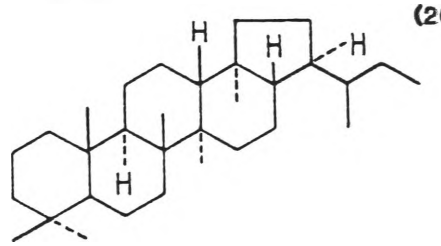


Table 16. continued

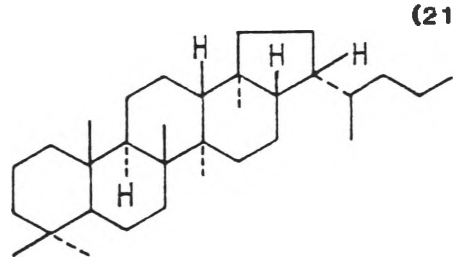
30	17βH,21βH-hopane $C_{30}H_{52}$	M=412,397,369,191*	Kimble *et al.*, 1974(a)(b); Wardroper *et al.*, 1977



31	17βH,21αH-homomoretane $C_{31}H_{54}$	M=426,205*,191 **(205/191 = 1.2)**	Wardroper *et al.*, 1977; Seifert & Moldowan, 1980



32 #	17βH,21βH-bishomohopane $C_{32}H_{56}$	M=440,219*,191 **(219/191 = 1.8)**	



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(1) Numbers refer to peaks in Figure 33; tentative identifications are indicated by #

(2) Electron impact ionisation; an asterisk indicates the base peak

Table 17. Branched/cyclic alkanes identified in the solvent extract from the carbonised oil shale

Peak[1] No.	Identity
1	2-methyldodecane
2	3-methyldodecane
3	2,6-dimethyldodecane
4	n-C_7 cyclohexane
5	2-methyltridecane
6	3-methyltridecane
7	2,6,10-trimethyldodecane
8	n-C_8 cyclohexane
9	2-methyltetradecane
10	3-methyltetradecane
11	n-C_9 cyclohexane
12	2-methylhexadecane
13	n-C_{10} cyclohexane
14	2-methylheptadecane
15	3-methylheptadecane
16	pristane
17	n-C_{11} cyclohexane
18	2-methyloctadecane
19	phytane

(1) Numbers refer to peaks in Figure 33

Creek shale. Squalene, a polyolefinic triterpene, which is frequently found in plant and animal tissue, is a possible precursor for many of the pentacyclic triterpenes. A scheme for the origin of the most important types of pentacyclic triterpanes from squalene is given in Figure 34. It is remarkable that squalene has survived the thermal conditions whereas no other triterpenoids were found in the carbonised shale.

The triterpenoid and steroid hydrocarbons were more abundant than the acyclic isoprenoid alkanes in the Kerosene Creek shale (Figure 33). No triterpenoid or steroid hydrocarbons were found in the carbonised oil shale. This is probably due to the thermal cracking reactions occurring on exposure to the igneous intrusion. This effect has also been observed in the Jurassic shales, Germany (Leythaeuser et al., 1980). No steranes or sterenes were detected in the Kerosene Creek shale although they have been detected in extracts of the Green River shale (Gallegos, 1971). The sample contained instead a series of 20R- and 20S-alkyl-substituted diacholestenes with carbon numbers C_{27} to C_{30} (Figure 33). These rearranged sterenes have not been reported to occur in living organisms and it is probable that their occurrence in the Kerosene Creek shale arises from dehydration and rearrangement of naturally occurring sterols in the geological environment. It has been shown that the major products of the thermal alteration of cholesterol incorporated into Green River shale were cholest-4-ene, cholest-5-ene and cholestane (Rhead et al., 1971); the isomers of 20R- and 20S-diacholestene have been produced in vitro by the backbone rearrangement of cholestenes

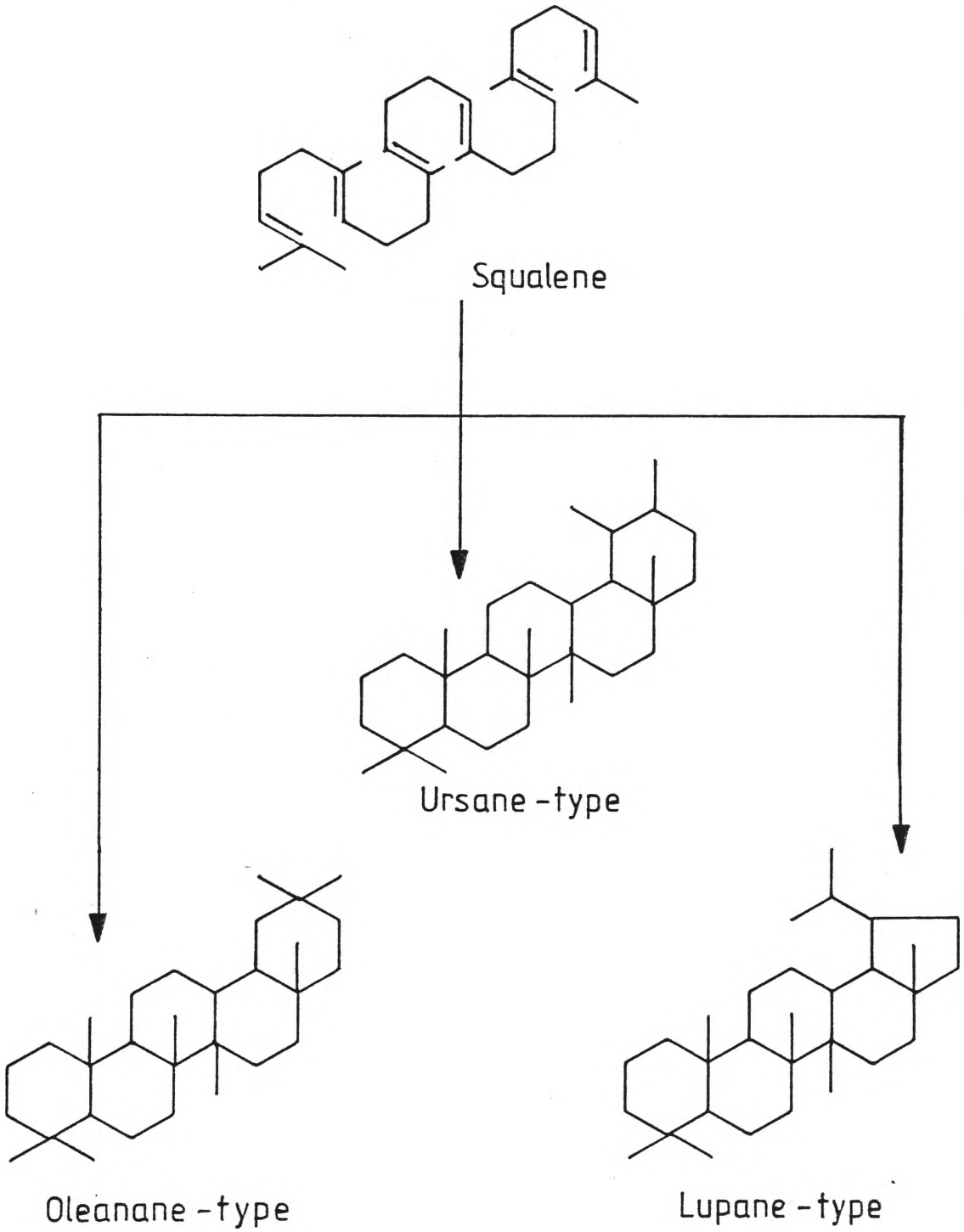


Figure 34. Pathway for the formation of different types of pentacyclic triterpanes from squalene

in the presence of acidic media (Blunt et al., 1969; Kirk and Shaw, 1970). Heating cholesterol with the clay montmorillonite also produces 20R-and 20S-diacholestenes (Rubinstein et al., 1975). No rearranged sterenes have been reported in extracts of the Green River shale. This may be explained by the greater proportion of carbonate minerals and lower proportions of silica and clay minerals in the inorganic matrix of this shale (Ingram et al., 1983; Hutton, 1983) which result in fewer sites for acid catalysis. A high content of steranes is often observed in marine sediments deposited in a reducing environment, with a high concentration of sulphur compounds. This observation may suggest that a very reducing and hydrogenating environment leads to steranes, whereas less reducing conditions of deposition lead to sterenes, which are subsequently converted to either aromatics or saturates.

Pentacyclic triterpenoids with carbon numbers C_{27} - C_{32} were identified in the Kerosene Creek shale (Figure 33) and their stereochemistry indicates that the sediment has never been subject to thermal stress. The reasons for this are as follows:

1: The thermodynamically unstable 17βH and 17βH, 21βH hopanes containing 27 and 32 carbon atoms respectively were detected in the extract. Hopanes with the 17βH, 21βH configuration occur in living bacteria (De Rosa et al., 1971; Rohmer, 1975) but are transformed by heating to the corresponding 17αH, 21βH isomers (Ensminger et al., 1974). The ratio (R_1) of the C_{27} 17βH-trisnorhopane to 17αH-trisnorhopane has been used as a maturity indicator for sediments where the ratio (R_1)

decreases as maturation increases (Kimble et al., 1974b; Seifert and Moldowan, 1978, 1980). In the sample extract, R_1 = 12, indicating only slight epimerization.

2. The ratio (R_2) of the C_{29} 17βH,21αH-normoretane to the more stable 17αH,21βH-norhopane is also correlated with the maturity of a sediment (Kimble et al., 1974b; Seifert, 1978; Seifert and Moldowan, 1978 and 1980). This ratio, (R_2), decreases as maturity increases. Here, R_2 = 4 suggesting the immaturity of the shale.
3. Three hopenes ($C_{30}H_{50}$), not identified, were major constituents of the triterpenoid hydrocarbons. Hopenes are synthesized by bacteria (De Rosa et al., 1971; Rohmer, 1975) and should be chemically reactive due to their unsaturation. Their presence in the sediment is consistent with a low-temperature predominantly anoxic environment.

Natural pentacyclic triterpenoids normally contain a C_{30} skeleton. Several points need explanation, i.e. the occurrence of triterpanes beyond C_{30} and the dealkylation of triterpanes from C_{27} to C_{29} in the Kerosene Creek shale.

Alkylation or dealkylation by microbial processes may result in an increase or decrease of the chain length by one or more carbon atoms (Bird et al., 1971a; Ensminger et al., 1972, 1974). On the other hand, the discovery of tetrahydroxybacteriohopane with C_{35} skeleton (Forster et al., 1973) may explain the occurrence of triterpanes greater than C_{30} (van Dorsselaer et al., 1974). Since Rohmer and Ourisson (1976) have shown that this class of compounds is ubiquitous in bacteria and blue-green algae, it seems probable that the hopane series with extended side chains is of prokaryotic

origin.

The C_{28} hopane is absent since its formation (like that of the C_{17} isoprenoid) would require cleavage of two carbon-carbon bonds.

(ii) Aromatic hydrocarbons

The mono- and diaromatic fraction in the Kerosene Creek shale constitutes 1% of the extractable organic matter (EOM) and contains di, tri, tetra and pentacyclic compounds aromatised in one or two rings (Figure 35, Table 18) whereas the carbonised shale contains predominantly substituted naphthalenes which constitutes 3% of EOM (Figure 35, Table 19). The polyaromatic hydrocarbon fraction in the Kerosene Creek shale (8% of EOM) contains tetra- and pentacyclic triterpenoids aromatised in three or four rings (Figure 36, Table 20) whereas the PAH fraction in the carbonised shale (4% of EOM) contains predominantly fully aromatised compounds with 3 - 5 rings (Figure 36, Table 21). The carbonised shale does not contain aromatised di-and triterpenoids, which occur in the Kerosene Creek shale, but fully aromatised compounds with 2 - 5 rings, such as naphthalenes, phenanthrenes, pyrenes and chrysenes, which are probably formed by thermal cracking of the di- and triterpenoids. The ring systems in the aromatic compounds of the Kerosene Creek shale resemble those in the corresponding saturated compounds (e.g. di- and triterpenoids) which are produced by living organisms and are presumably derived from them by aromatisation and rearrangement. The problem is to explain the occurrence of these processes in the Kerosene Creek shale which is known from its geology to have experienced little heating.

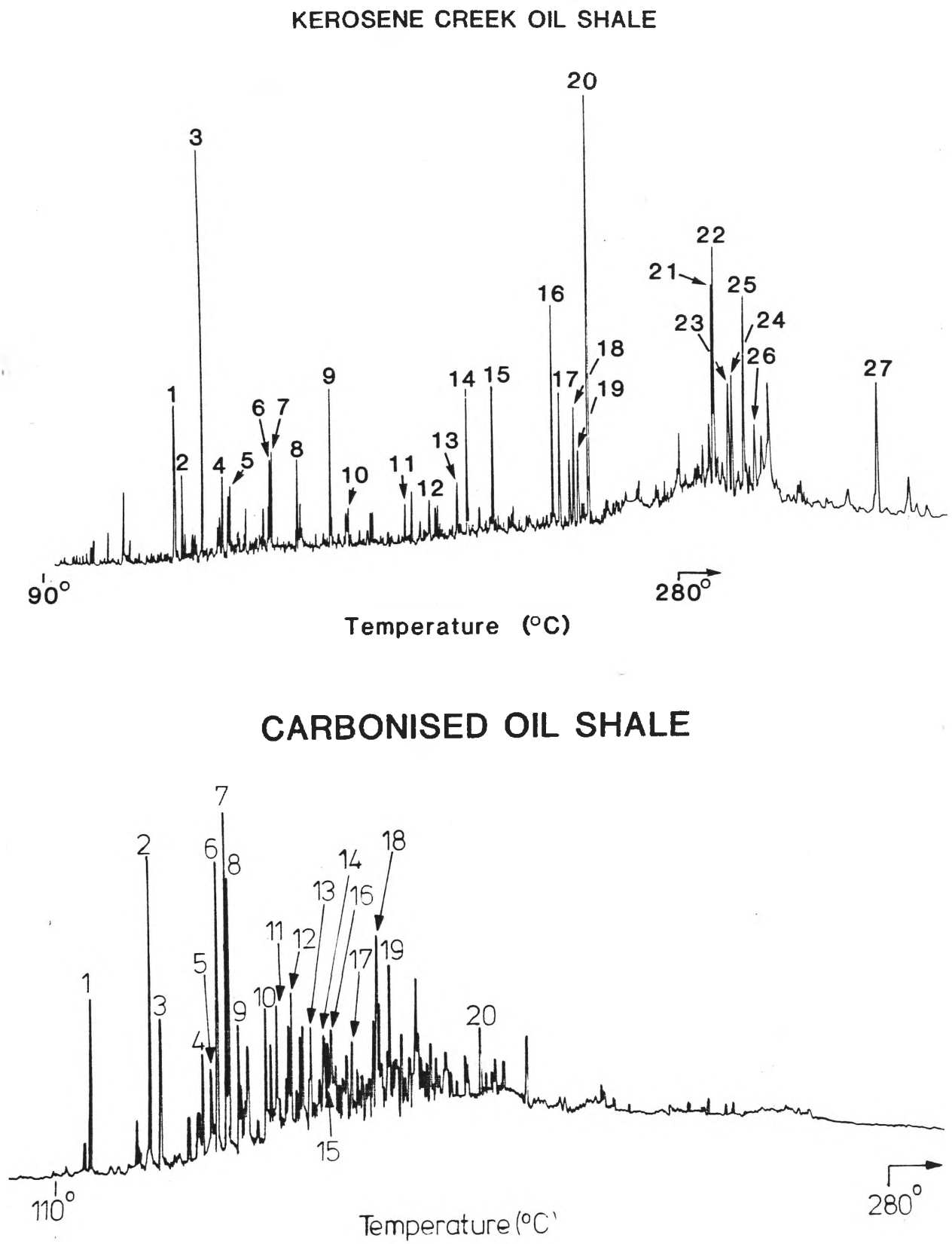


Figure 35. Gas chromatograms of the mono- and diaromatic hydrocarbon fractions from the solvent extracts of the Kerosene Creek and carbonised oil shales. Numbers in the gas chromatograms of the Kerosene Creek and carbonised oil shales refer to compounds in Table 18 and 19 respectively.

Table 18. Mono- and diaromatics identified in the solvent extract from the Kerosene Creek oil shale

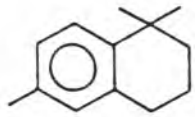
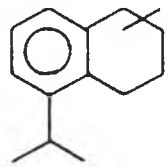
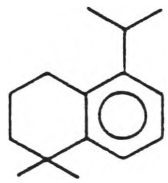
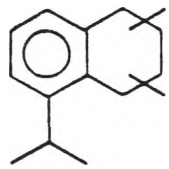
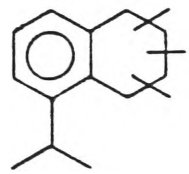
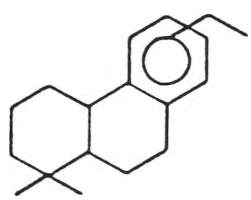
Peak No.[1]	Identity	Characteristic Ions[2]	Reference
1	2-methylnaphthalene	M=142*,141	Stenhagen *et al.*, 1974
2	1-methylnaphthalene	M=142*,141	
3	ionene	M=174,159*	
			
4≠		M=188,173*,131	
5	2,6-dimethylnaphthalene	M=156*,141,155,157	
6	$C_{16}H_{22}$	M=214,199*	
7≠		M=202,159*,144,131	
8≠		M=202,187*,159,145,131	
9	1,6-dimethyl-4-isopropyl naphthalene	M=198,183*,168,153	
10≠		M=212,197*,155	
11≠		M=242,227*,171,158, 145,131	

Table 18. continued

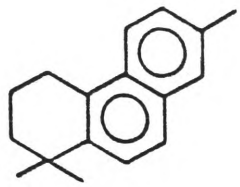
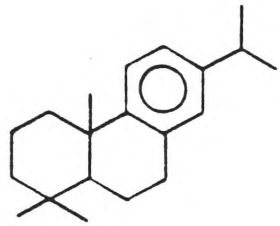
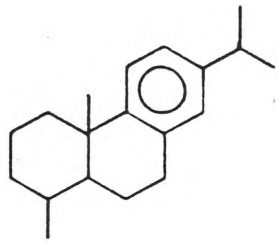
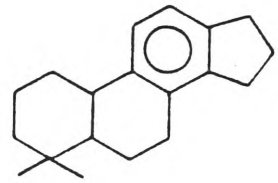
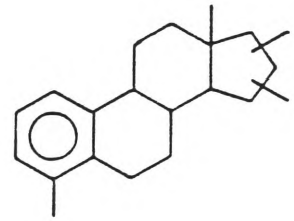
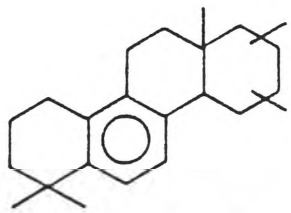
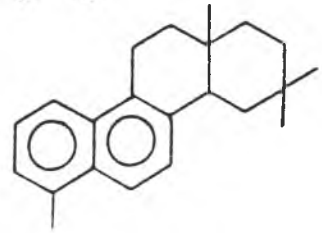
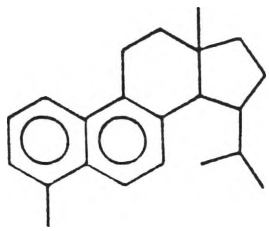
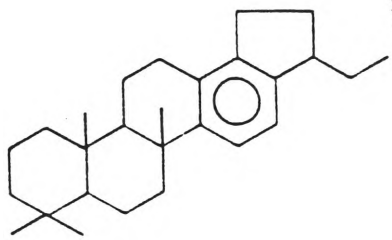
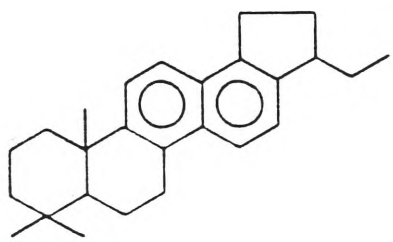
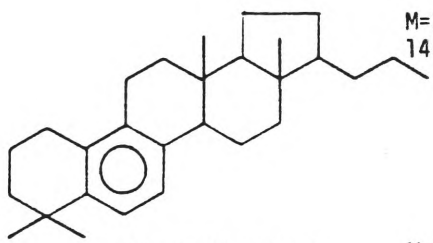
12#		M=224,209*	
13	dehydroabietane	M=270,255*,185,173,159	Stenhagen *et al.*, 1974
			
14#		M=254,241,199,185,171, 159,145*	
15#		M=254*,239,226,211,197, 183,171,157,143,131	
16#		M=282*,158,143,131	
17#		M=310,295*,171,157,145, 137,131	
18		M=292*,277,235,221, 207,193,168	Spyckerelle *et al.*, 1977b.

Table 18. continued

19		M=292,249,209,208, 207*,193,178	Laflame and Hites, 1979
20	isomer of peak 17	M=310,295*,171,157, 145,137,131	
21		M=364,349,335,225,211*, 199,185,157,145,137	Greiner *et al.*, 1977
22	$C_{28}H_{40}$	M=376,361,172,158,145*	
23	$C_{28}H_{40}$	M=376,361,158,145*	
24	$C_{28}H_{42}$	M=378,172,157,145*	
25		M=346*,331,317,261, 235,179	Greiner *et al.*, 1977
26#		M=378,363,171*,157 145,137	
27	pentacyclic triterpane aromatized in ring A or B	M=418,393,197*, 183,158,137	

(1) Numbers refer to peaks in Figure 35; tentative identifications are indicated by #

(2) Electron impact ionisation; an asterisk indicates base peak

Table 19. Diaromatics identified in the solvent extract from the carbonised oil shale

Peak No.[1]	Identity
1	naphthalene
2	2-methylnaphthalene
3	1-methylnaphthalene
4	biphenyl
5	ethylnaphthalene
6	2,6-dimethylnaphthalene
7	dimethylnaphthalene
8	isomers
9	2,3-dimethylnaphthalene
10	methylbiphenyl
11	isopropylnaphthalene
12	trimethylnaphthalene
13	isomers
14	1-tert.-butylnaphthalene trimethylnaphthalene
15	3,3'-dimethylbiphenyl or 3,4'-dimethylbiphenyl
16	1-propyl-2-methylnaphthalene
17	unknown (m/e 187 (base peak), 172, M^+202)
18	unknown (m/e 184 (base peak, M^+), 169, 153)
19	unknown (m/e 195 (base peak), 181, 165, M^+210)
20	unknown (m/e 210 (base peak, M^+), 196, 181

(1) Numbers refer to peaks in Figure 35

β-Carotene (Figure 37) has been suggested as the precursor of ionene and other naphthalene derivatives (Table 18, compounds 1 - 10; Day and Erdman, 1963) and its conversion into these compounds has been demonstrated in the laboratory at temperatures as low as 100°C (Ikan et al., 1975b). Carotenoids are ubiquitous in nature (Jensen, 1962) and perhydro-β-carotene has been identified in the Green River shale (Murphy et al., 1967; Gallegos, 1971). Decomposition of carotenoids may occur at temperatures much lower than 100°C in the presence of mineral catalysts over geological time.

Dehydroabietane and compounds of similar structure (Table 18, compounds 11-14) appear to be derived from abietic acid, a common diterpenoid acid in the resins of higher plants (Simoneit, 1977; Laflame and Hites, 1978). Retene (7-isopropyl-1-methylphenanthrene), which is believed to arise from complete aromatisation of abietic acid (Figure 38) (Wakeham et al., 1980a; Simoneit, 1977), was not detected in the Rundle shale. This would suggest that the Kerosene Creek oil shale was not subjected to very strong reducing conditions.

Pentacyclic triterpenoid compounds often are major constituents of higher plant waxes and are believed to be important source materials for aromatic hydrocarbons. Hopane-related PAH progressively aromatised from one to four rings were identified in the Kerosene Creek shale (Tables 18, 20). These are most probably derived from hopane derivatives by loss of one of the carbon atoms of the side chain and progressive aromatisation starting with ring D through to ring A (Greiner et al., 1976).

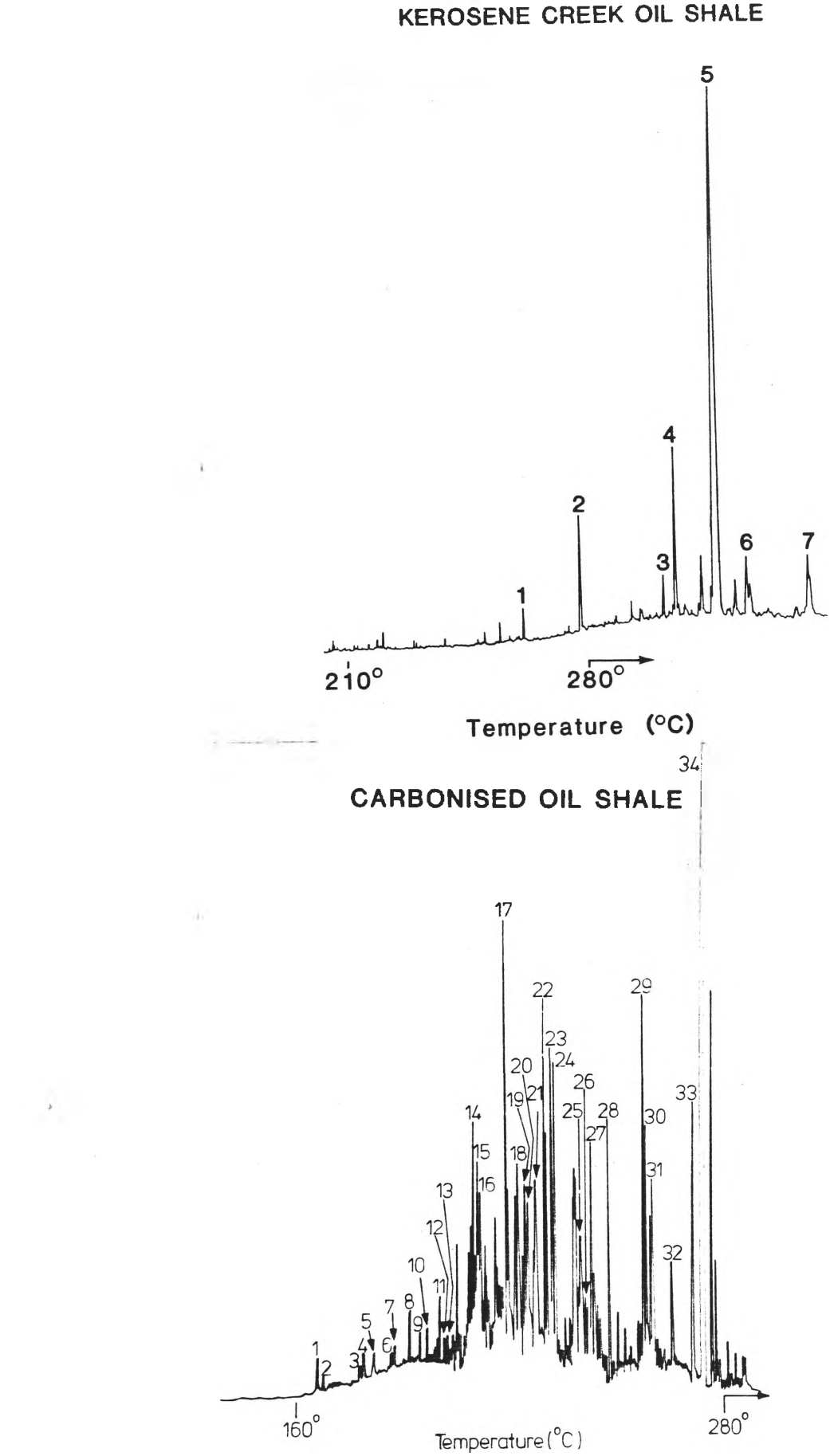


Figure 36. Gas chromatograms of the polyaromatic hydrocarbon fractions from the solvent extracts of the Kerosene Creek and carbonised oil shales. Numbers in the gas chromatograms of the Kerosene Creek and carbonised oil shales refer to compounds in Table 20 and 21 respectively.

Table 20. Polyaromatics identified in the solvent extract from the Kerosene Creek oil shale

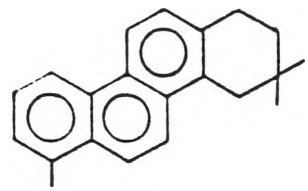
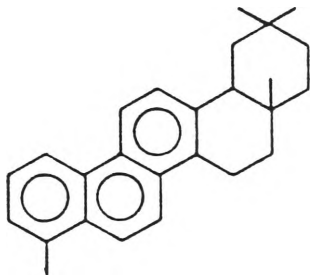
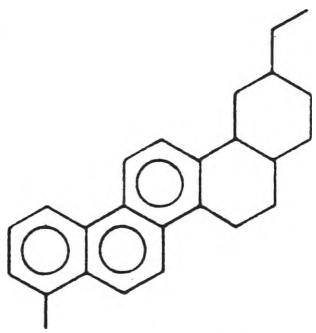
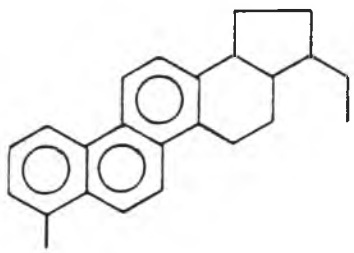
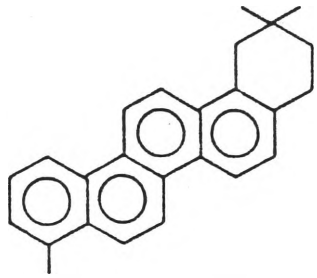
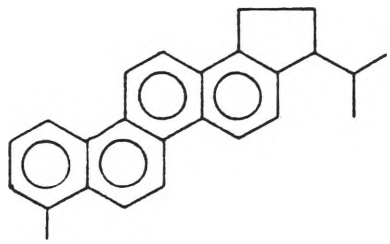
Peak No.[1]	Identity	Characteristic Ions[2]	Reference
1	3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene 	M=274,218*,202	Spyckerelle *et al.*, 1977(a); Laflame and Hites, 1979: Wakeham *et al.*, 1980a, 1980b.
2	perylene	M=252*	Stenhagen *et al.*, 1974
3	2,2,4a,9-tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene 	M=342*,257,218,205, 231	Laflame and Hites, 1979; Wakeham *et al.*, 1980a, 1980b.
4#		M=328,313,299*,257,229	
5	7-methyl-3'-ethyl-1,2-cyclopentanochrysene 	M=310,281*,266,252	Laflame and Hites, 1979; Wakeman *et al.*, 1980a, 1980b.

Table 20. continued

6	2,2,9-trimethyl-1,2,3,4-tetrahydropicene	M=324,268*,252	Laflame and Hites, 1979; Wakeham *et al.*, 1980a, 1980b.



7	7-methyl-3'-propyl-1,2-cyclopentanochrysene	M=324,295*,280	



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(1) Numbers refer to peaks in Figure 36; tentative identifications are indicated by #

(2) Electron impact ionisation; an asterisk indicates base peak

Table 21. Polyaromatics identified in the solvent extract from the carbonised oil shale

Peak No.[1]	Identity
1	fluorene
2	9-methylfluorene
3, 4	methylfluorene isomers
5	dimethylfluorene
6	phenanthrene
7	anthracene
8, 9	ethylfluorene
10	dimethylfluorene
11, 12, 13	methylphenanthrene isomers
14, 15, 16	dimethylphenanthrene isomers
17	pyrene
18, 19, 20	trimethylphenanthrene isomers
21	1,2-benzofluorene
22	2,3-benzofluorene
23, 24	methylpyrene
25, 26, 27	ethylpyrene and/or ethylfluoranthrene
28	chrysene or 1,2-benzanthrene
29, 30, 31	methylchrysene and/or methylbenzophenanthrene and/or methylbenzoanthracene
32	benzopyrene
33	perylene
34	squalene

(1) Numbers refer to peaks in Figure 36

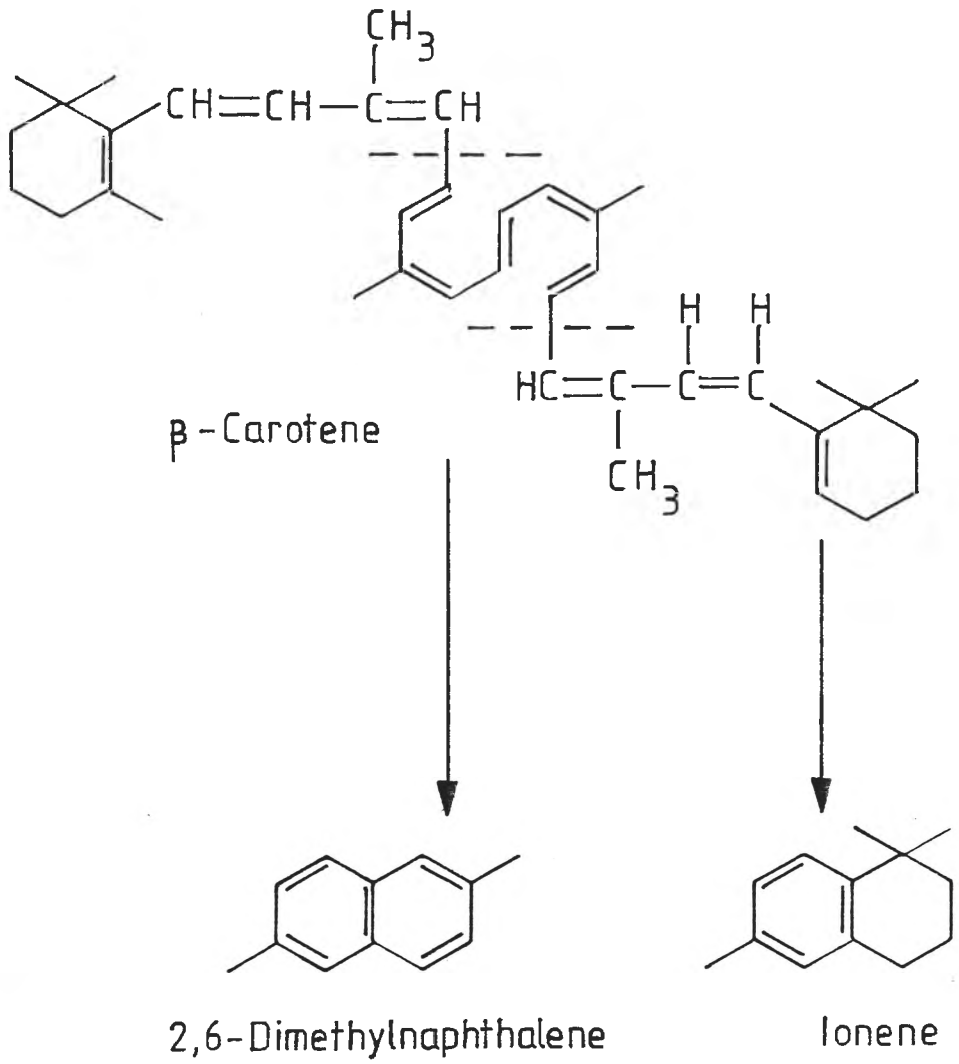


Figure 37. Proposed pathway for the formation of 2,6-dimethylnaphthalene and ionene from β-carotene. (Ikan et al., 1975b)

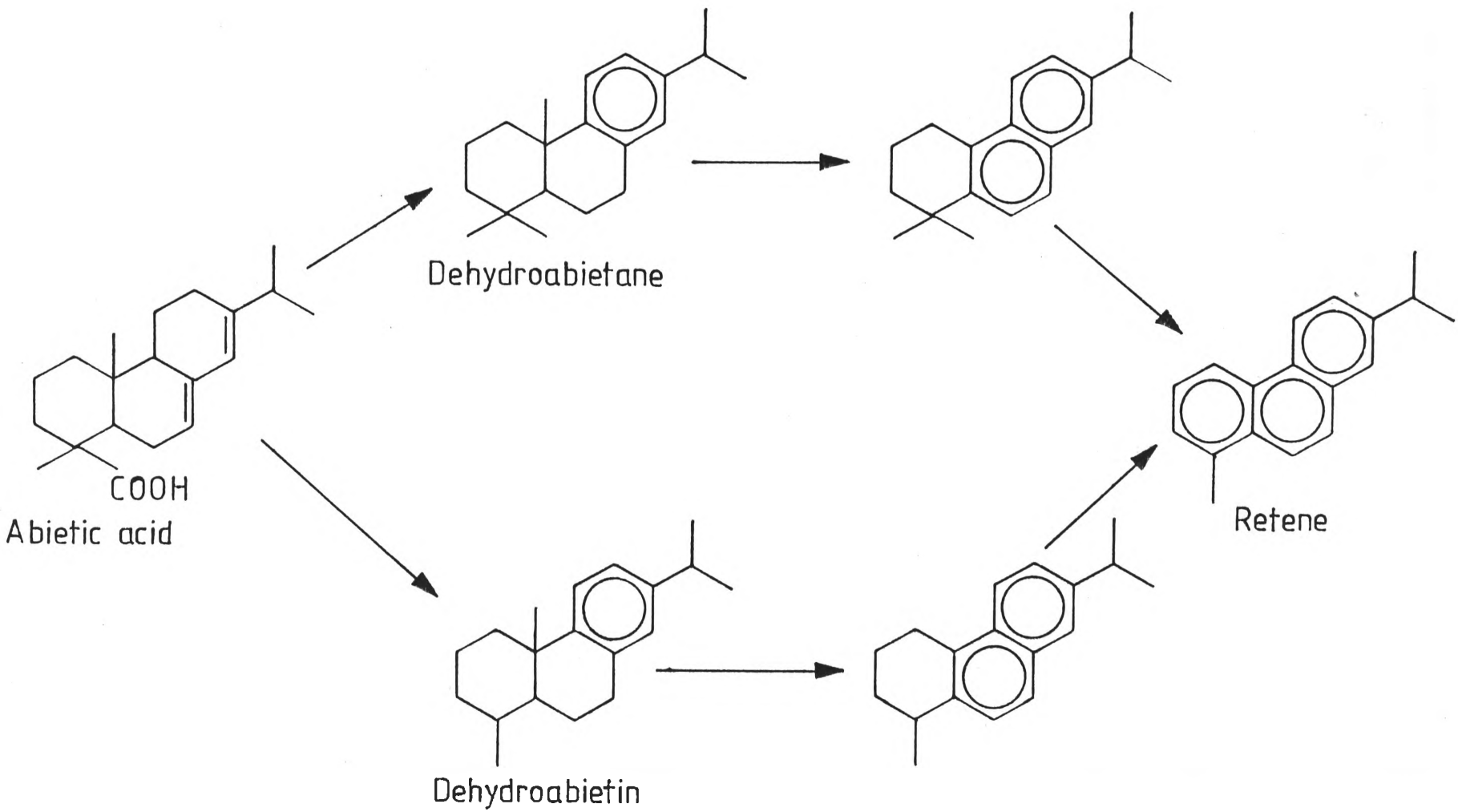


Figure 38. Proposed pathway for the formation of abietic acid derived compounds (Wakeham et al., 1980a)

The pentacyclic picene and tetracyclic chrysene derivatives identified in the Kerosene Creek shale may be derived from triterpenoids with a six-membered E-ring (e.g. amyrin, Figure 39) which are common constituents of higher plant waxes (Spyckerelle et al., 1977a, b; Laflame and Hites, 1979). Under conditions enabling dehydrogenation, aromatisation of pentacyclic triterpenes may start in the A-ring and proceed through the D- and E-rings. If aromatisation begins by loss of the oxygen function in the A-ring, picene derivatives are formed. If the reaction is initiated by cleavage of the A-ring and aromatisation begins in the B-ring, then the chrysenes are formed (Figure 39). Corbet et al. (1980) postulated that ring A is lost by oxidation of the 3-alcohol to the corresponding 3-ketone and subsequent photomimetic or photochemical process (Figure 40). Photomimetic products are formed by microorganisms through biochemical reactions leading to the 3-ketones in their excited state (either by energy transfer or by oxidation of the 3-alcohol to the excited ketone).

Aromatic compounds similar to those reported in the Kerosene Creek shale have been identified in immature Messel and Menat shales (Eocene, lacustrine; Greiner et al., 1977), from Yallourn lignite (Miocene, Australian pollen coal; Spyckerelle et al., 1977a, b) and from Recent sediments (Laflame and Hites, 1978, 1979; Wakeham et al., 1980a, 1980b). Aromatisation processes appear to occur at low temperatures in sediments at an early stage of diagenesis (Ensminger et al., 1972). In addition to the mechanisms already proposed, it is possible that some aromatisations are carried out by diverse

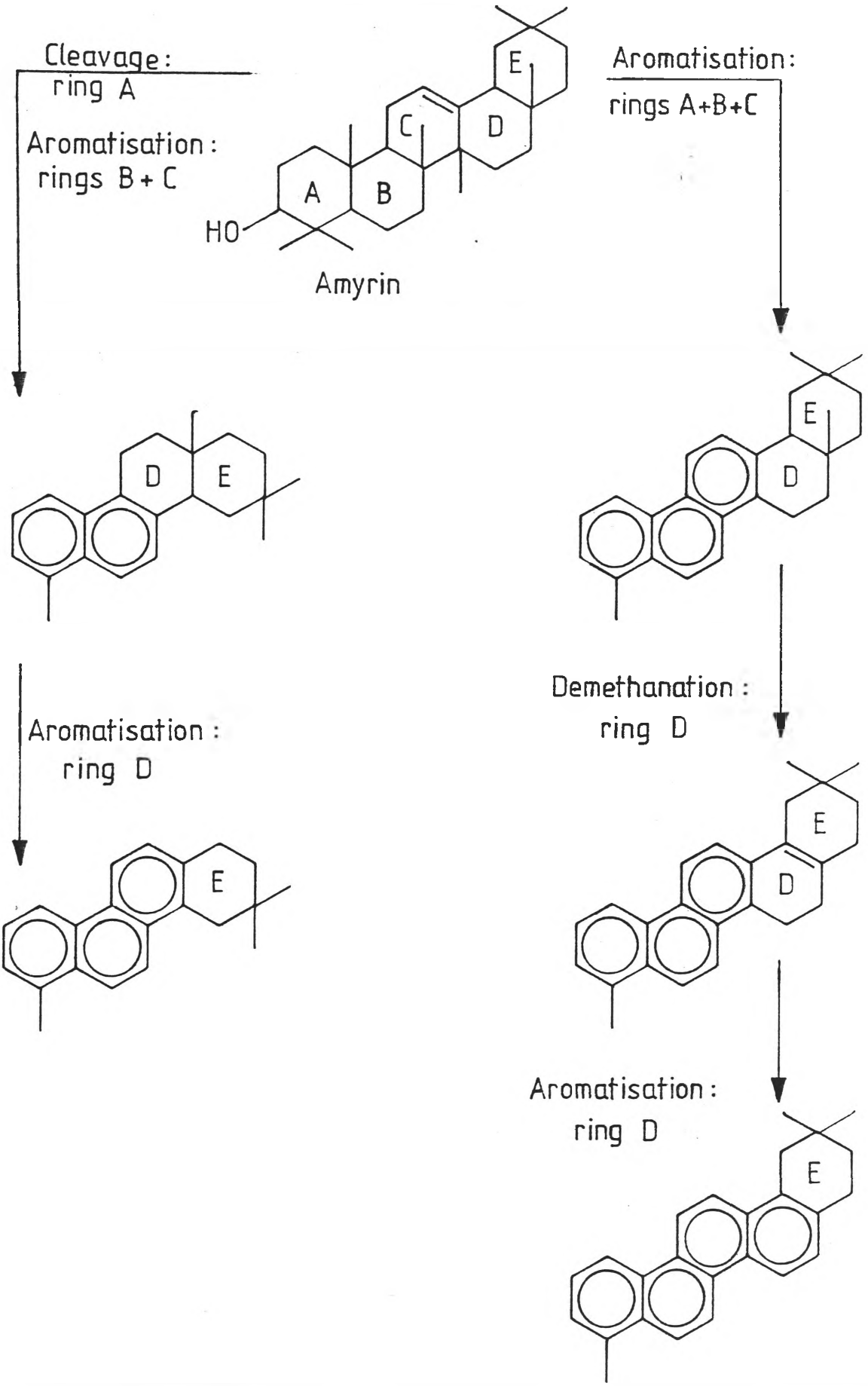


Figure 39. Hypothetical aromatisation scheme for amyrin (Laflame and Hites, 1979)

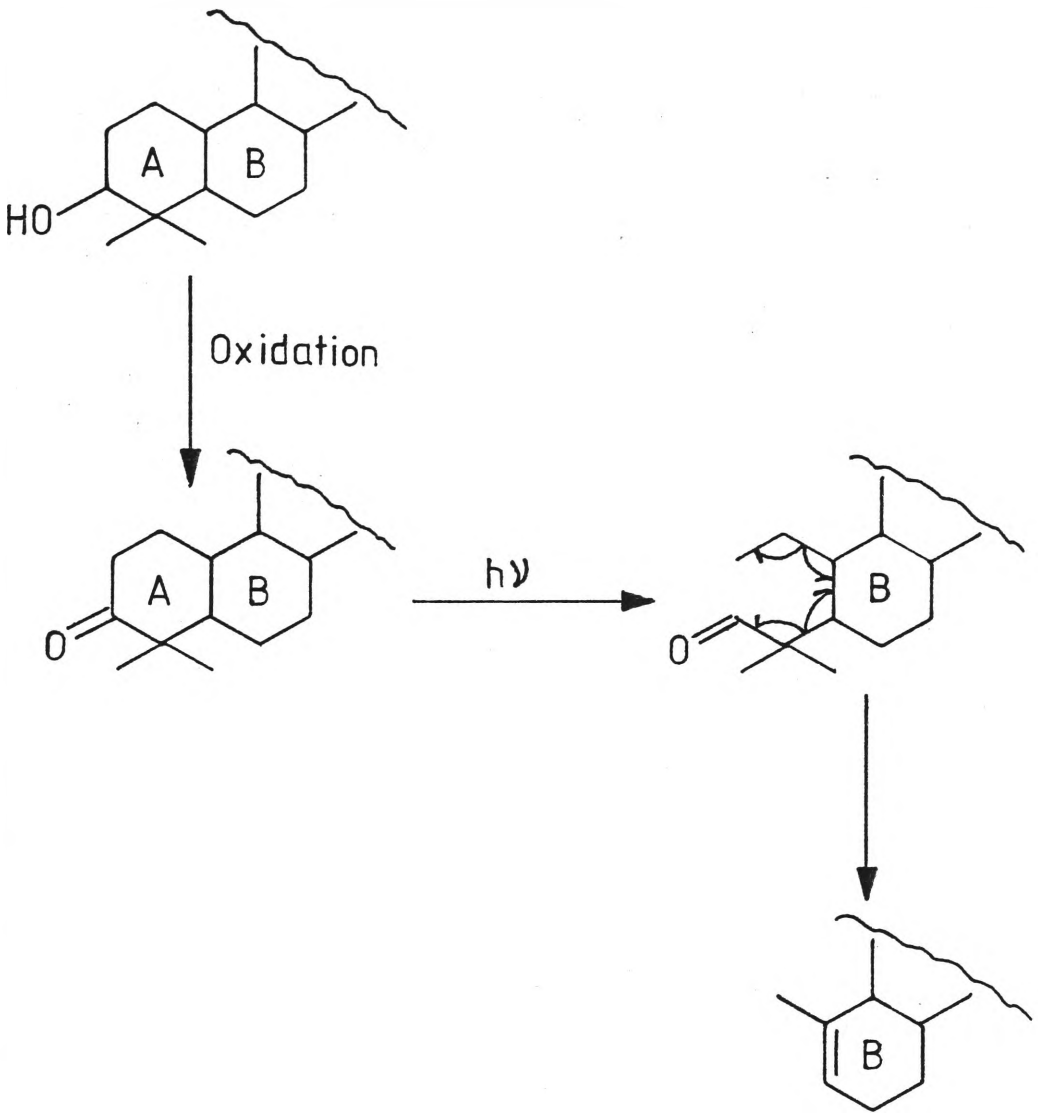


Figure 40. Proposed pathway for the cleavage of ring A (Corbet et al., 1980)

species of hydrogen-consuming bacteria, some of which are able to use nitrate instead of oxygen as electron acceptor (Gottschalk, 1979). Such bacteria are difficult to study and no experimental evidence for this is yet available.

(iii) Aliphatic, steroid and triterpenoid alcohols

The solvent extract from the Kerosene Creek shale contained linear 1-alkanols (C_9 - C_{30}, maximum C_{28}, even carbon number preference) and 2-alkanols (C_{13} - C_{31}, maximum C_{29}, odd carbon number preference) which together accounted for $\leq$1% of EOM (Figure 41). Although linear, branched-chain and isoprenoid alcohols are abundant in nature, this functional group class has been rarely reported in sediments. The alcohol components of plant waxes are linear and saturated (C_{22} - C_{32}) (Eglinton and Hamilton, 1967; Wollrab and Streibl, 1969; Kollattukudy, 1971). Eglinton and Hamilton (1967) have reported the presence of primary alcohols with even carbon number preference and secondary alcohols with odd carbon number preference in plant waxes. A possible explanation for this pattern of carbon number preference may be that the alcohols are biosynthesised by direct reduction of even-numbered fatty acids to primary alcohols, whereas the odd-numbered members could be formed from fatty acids by the sequence β-oxidation, decarboxylation and reduction.

Steroid alcohols occur widely as minor constituents of plants and animals. They are usually unsaturated (stenols), with cholesterol being a particularly common example. Stanols such as cholestanol and ergostanol have been found in sediments, together with stenols, which have been found in living algae

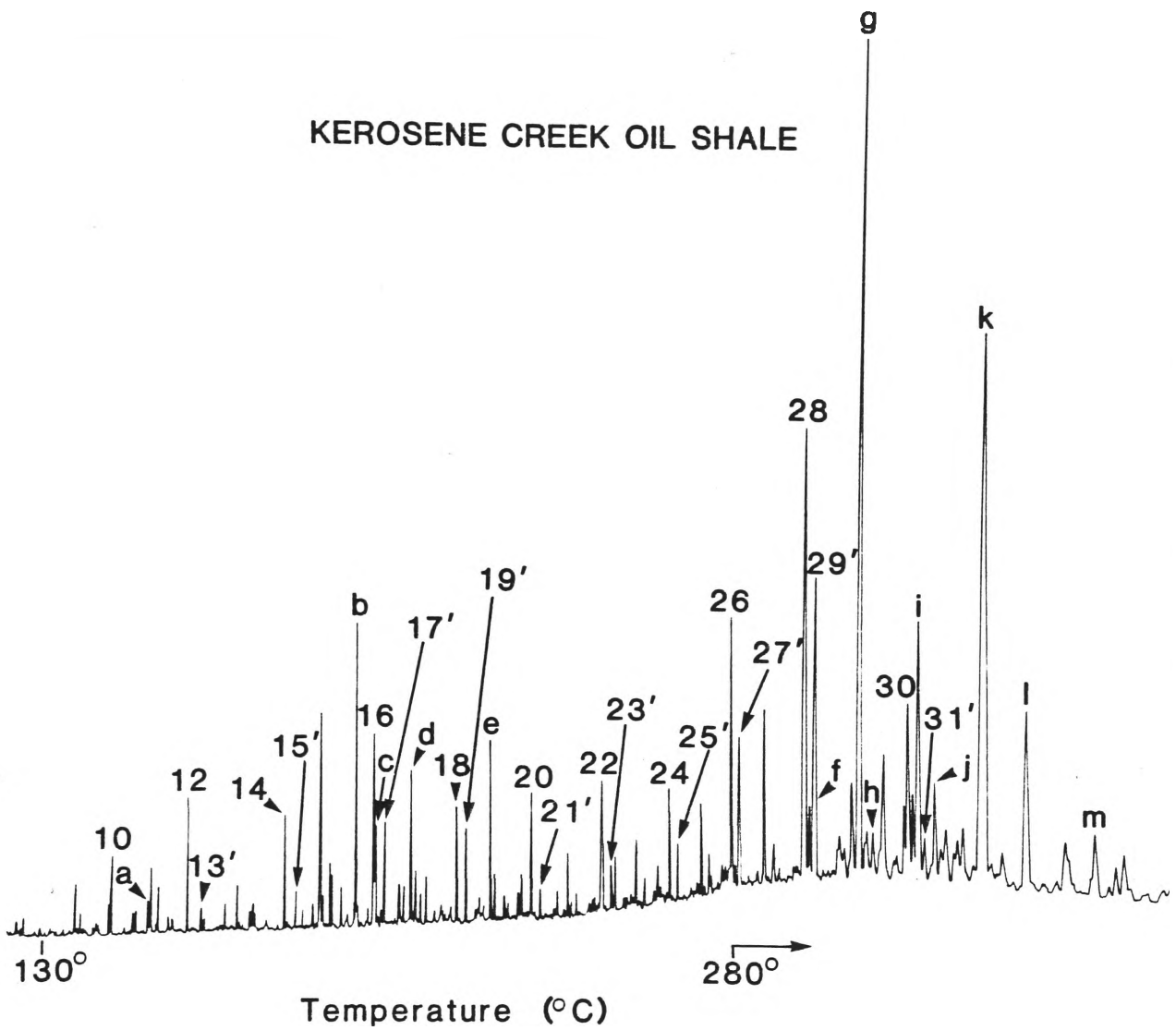
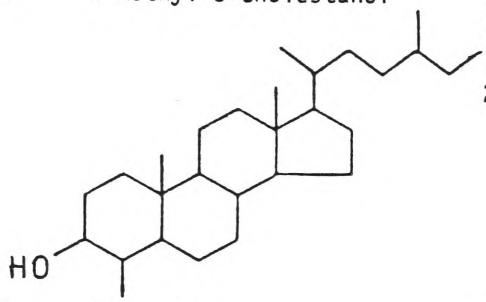
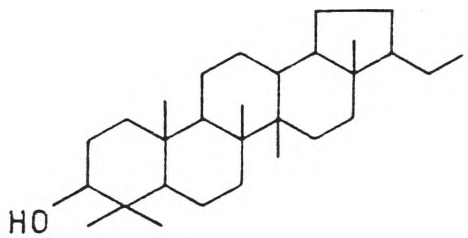


Figure 41. Gas chromatogram of the aliphatic and steroidal alcohol fraction from the solvent extract of the Kerosene Creek oil shale. Carbon numbers are indicated for homologous 1-alkanols (no prime) and 2-alkanols (with prime). Letters refer to compounds in Table 22.

Table 22. Aliphatic, steroid and triterpenoid alcohols identified in the solvent extract from the Kerosene Creek oil shale

Peak No.[1]	Identity	Characteristic Ions of[2] TMS derivatives	Reference
a#	4-alkenol $C_{13}H_{25}OH$	M=270,255,145*,73,75	
b	branched 2-alkanol $C_{18}H_{37}OH$	M=342,327,299,117*,73,75	
c	branched 3-alkanol $C_{19}H_{39}OH$	M=356,341,299,131*,73,75	
d	branched alkanol $C_{17}H_{35}OH$	M=328,313,145,132,117,75, 73*	
e	branched alkanol $C_{19}H_{39}OH$	M=356,341,145,132,117,75, 73*	
f	stanol $C_{28}H_{49}OH$	M=474,459,384,369,345, 229,75*,73	
g #	4-methyl-3-cholestanol	M=474,459,384,369 345*,229,75 (M=402,387,385,369,262, 247,229*,179)	Diekman and Djerassi, 1967
h#	$C_{29}H_{49}OH$	M=486,471,396,381, 191*,189,75,73	Henderson and Steel, 1971
i#	4-methyl-3-ergostanol	M=488,473,397,383, 359,229,75* (M=416,401,383,262, 247,229*,179)	Diekman and Djerassi, 1967





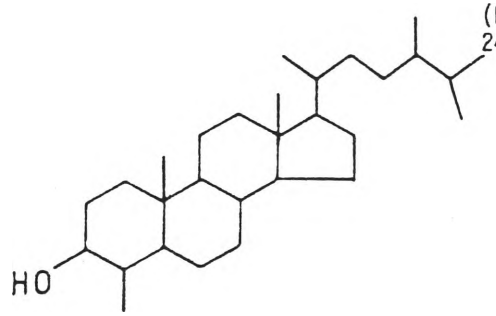
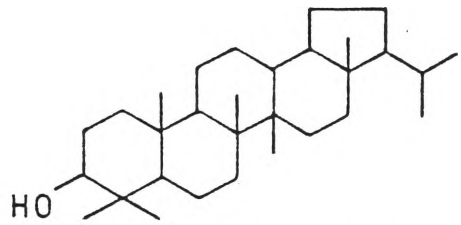
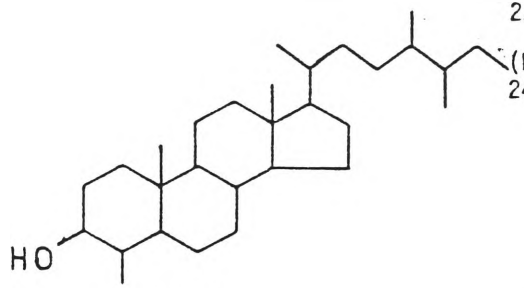
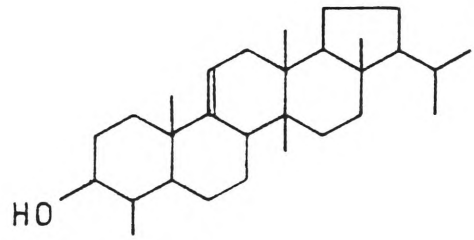
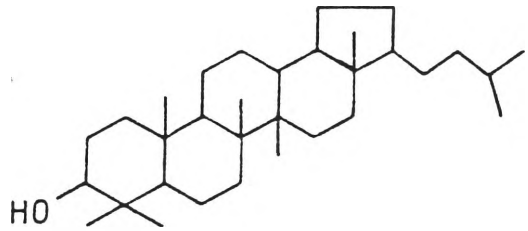


Table 22. continued

j#	$C_{30}H_{51}OH$ 	M=500,485,410,395, 191,189,75,73	Henderson and Steel, 1971
k#	4-methyl-3-stigmastanol 	M=502,487,412,397,373*, 229,75 (M=430,415,412,397,262, 247,229*,179)	Diekman and Djerassi, 1967
l	fernenol 	M=498,483,393,255 241,191,189,75,73* (M=426,411,393,273, 259*,241)	Nishimoto *et al.*, 1968.
m#	$C_{32}H_{55}OH$ 	M=528,513,438,423, 191*,189,75,73	

(1) Letters refer to peaks in Figure 41; tentative identifications are indicated by #

(2) Electron impact ionisation; an asterisk indicates base peak; characteristic ions of underivatized compounds indicated by parentheses

(Attaway and Parker, 1970; Mattern et al., 1970; Henderson et al., 1971; Steel and Henderson, 1972). No stenols were detected, but a number of stanols were found in the Kerosene Creek shale (most probably 4-methyl-3-stanols, C_{28} - C_{30}, C_{28} most abundant; Figure 41; Table 22). Because the saturated stanols are much less abundant in living matter than the unsaturated stenols, it is likely that they are derived by microbiological reduction of the latter after burial (Gaskell and Eglinton, 1975, 1976). Microorganisms can transform stenols into stenones and stanones and finally to stanols (Rosenfeld and Hellman, 1971). Stanols resist oxidative degradation better than stenols (Nishimura, 1978). 4-Methylstanols are not very abundant in sediments although the 4-methylstenols are abundant in certain prokaryotes and have been reported in sediments (Mattern et al., 1970; Bird et al., 1971b). It seems likely that the 4-methylstanols apparent in the Rundle shale are a result of microbial activity.

Pentacyclic triterpenoid alcohols (C_{29} - C_{32}; Figure 41 ; Table 22) were found in trace amounts and may be the precursors of the more abundant hopane hydrocarbons into which they can be converted by reduction. The unsaturated alcohol, fernenol, was the most abundant member of this group.

(iv) Ketones

No steroid or triterpenoid alcohols were detected in the carbonised shale. Instead, a homologous series of methyl ketones was detected ranging from C_7 - C_{19} with a maximum at C_{14} and even carbon number preference in the region C_{10} - C_{19}, as well as smaller amounts of ethyl ketones, C_{11} - C_{19}

with a maximum at C_{14} and even carbon number preference in the region C_{14} - C_{17}. Only trace amounts of 1-alcohols were detected in the carbonised shale. Because of the small amount of the carbonised shale being available, only limited data was obtained from this fraction. Figure 42 represents the single ion chromatogram from the mass spectrometer of the methyl and ethyl ketones and of a series with a characteristic m/e 80 (base peak) and m/e 79. This unknown series did not produce molecular ions and because of the extremely small amount of the fraction extracted (< 1mg), these compounds could not be identified.

(v) Porphyrins

Metal-free porphyrins were identified, on the basis of their mass spectra, in the solvent extract of the Kerosene Creek shale, whereas nickel-porphyrins were detected in the carbonised shale (Figure 43). It appears that there are five homologous series of metal-free porphyrins in the Kerosene Creek shale, with a further two homologous series tentatively identified as porphyrins. The most abundant porphyrins were of the deoxophylloerythroetioporphyrin (DPEP) and etioporphyrin (Etio) types ranging from C_{25} to $\geqslant C_{39}$ in the Kerosene Creek shale and up to $\geqslant C_{35}$ in the carbonised carbon. The Etio type porphyrin is the dominant type. Unfortunately, the computer software at the time was only capable of scanning up to m/e 576. The molecular weights of metal-free porphin and nickel porphin are 310 ($C_{20}H_{14}N_4$) and 368 respectively and alkyl substituted etioporphyrin must fall in the series 310 + 14n and 368 + 14n, where n is an integer. Likewise, porphyrins with an isocyclic ring (DPEP series) must have molecular weights of 308 + 14m and 366 + 14m,

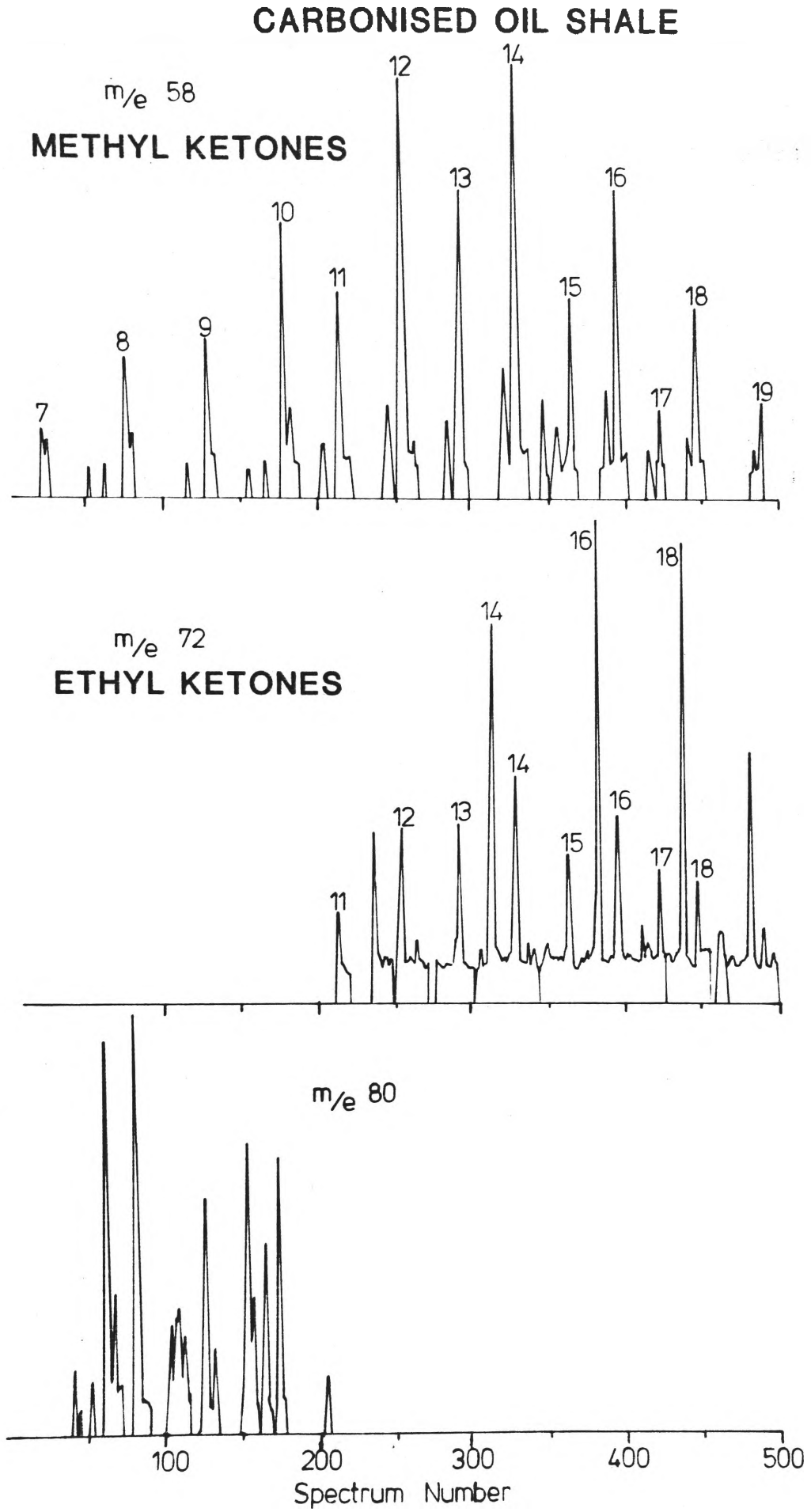
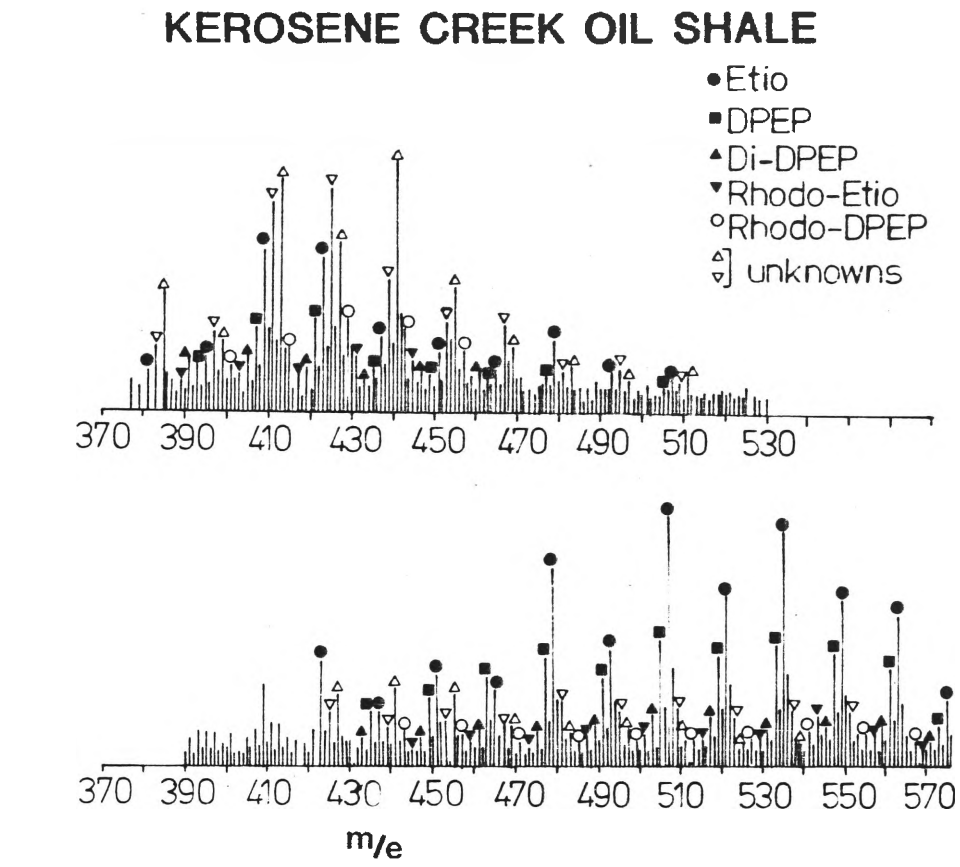


Figure 42. Single ion chromatograms of the ketone fraction from the carbonised oil shale. Carbon numbers are indicated.

where m is an integer 2 or greater. Minor amounts of three other types (Di-DPEP, Rhodo-Etio and Rhodo-DPEP; Barwise and Whitehead, 1980) with carbon numbers C_{25} to $\geqslant C_{39}$ were identified in the Kerosene Creek shale. No Rhodo porphyrins were identified in the carbonised shale. For the same carbon number, the Di-DPEP type has 2 hydrogens less than the DPEP, suggesting the possibility of two isocyclic rings attached to the porphyrin skeleton while Rhodo-Etio and Rhodo-DPEP has 6 hydrogens less than the corresponding Etio and DPEP types, indicating the possibility of a benzene ring attached to the porphyrin skeleton (Barker et al., 1967; Shaw et al, 1978; Barwise and Whitehead, 1980). The two tentatively identified porphyrin series in the Kerosene Creek shale have molecular weights, six less than the Rhodo-Etio and Rhodo-DPEP series respectively and have not been reported previously. They may be related to these series by addition of another fused benzene ring to the porphyrin system.

The porphyrins in the carbonised shale with molecular weights of m/e 464 to 576 are nickel Etio and DPEP porphyrins with the Etio being the dominant porphyrin. Below m/e 464 it is difficult to predict whether these are also nickel porphyrins since the molecular weights also correspond to the metal-free Etio and DPEP porphyrins. The molecular weight of unsubstituted nickel porphyrin is 368 and according to the chemical ionization impact mass spectra (Figure 43), there are molecular ions below m/e 368. The unsubstituted metal-free porphin has a molecular weight of 310. Again, there are molecular ions below m/e 310. This would suggest that the carbonised shale has only nickel porphyrins or a combination of metal-free and



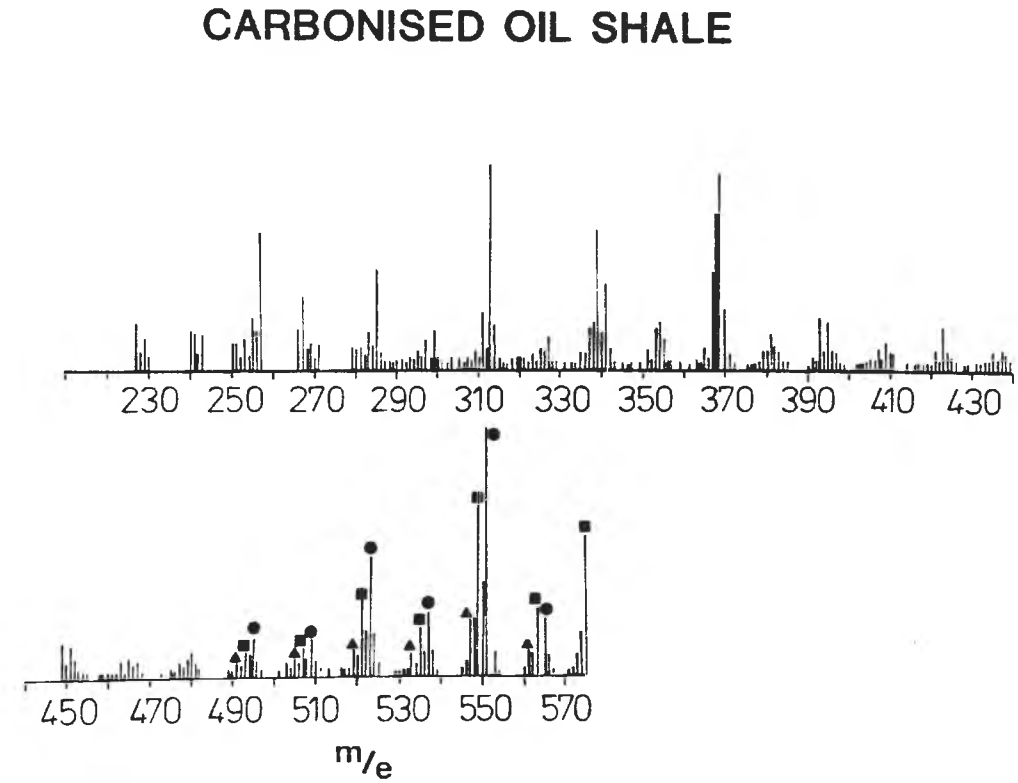


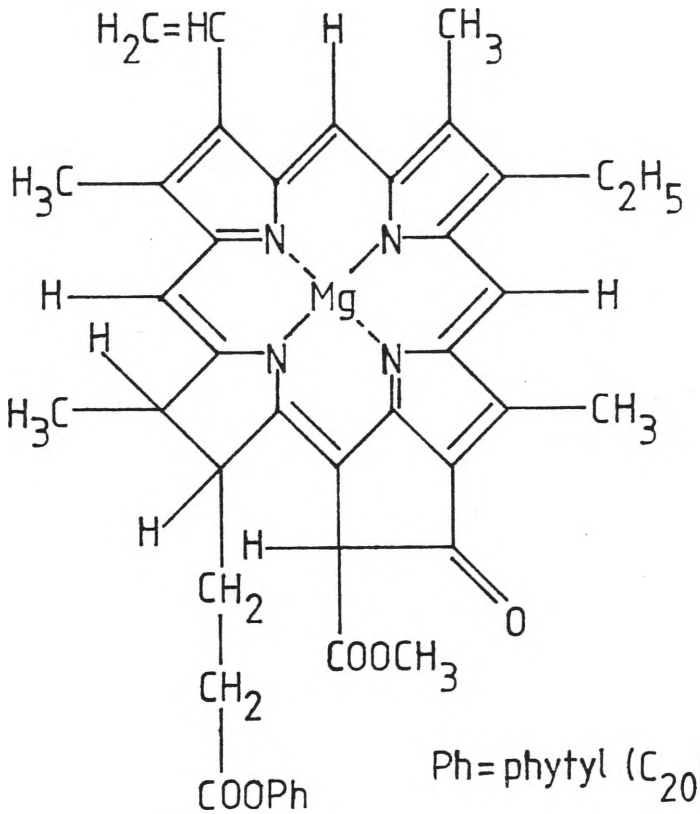
Figure 43. Mass spectra of porphyrins from the Kerosene Creek and carbonised oil shales using chemical ionisation mass spectrometry

nickel prophyrins. Also it appears that the ions produced by the chemical ionisation impact are not molecular ions but fragmentation ions due to the direct-insertion technique. This fragmentation of porphyrins by the direct-insertion technique in the mass spectrometer has been observed previously (Dr. Ekstrom personal communication). An alternative technique for analysing porphyrins by the mass spectrometer is the fast atom bombardment (FAB) technique where the material is bombarded with fast atoms rather than electrons. It appears that this (FAB) technique produces molecular ions of the porphyrins rather than fragmentation ions.

Treibs (1936) identified the basic porphyrin fraction from bitumens as spectroscopically identical with desoxophyllo-erythrin and concluded from elemental analysis that the material was DPEP. Making the assumption that the precusor was chlorophyll a (Figure 44), Treibs explained that the C_{32} DPEP resulted from a sequence of degradative steps as follows.

(1) magnesium loss
(2) ester hydrolysis, presumably under acidic conditions, since alkaline hydrolysis would also open the isocyclic ring
(3) hydrogenation of the vinyl group
(4) dehydrogenation of the green (chlorin) system to the red (porphyrin) system
(5) reduction of the 9-carbonyl group to CH_2
(6) decarboxylation and
(7) chelation

Chlorophyll a



DPEP

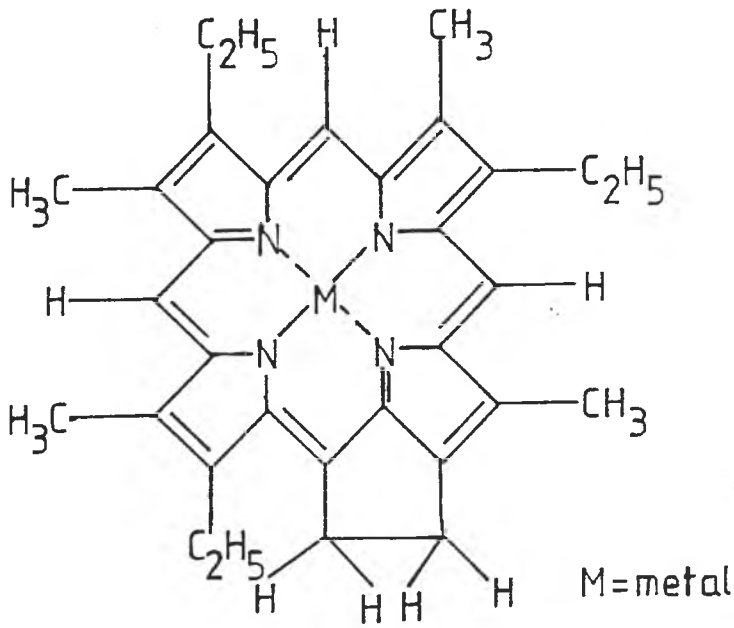


Figure 44. Structures of chlorophyll a and C_{32} DPEP (Treibs, 1936)

This does not explain the large spread in alkylation ($> C_{32}$) with the porphyrins. Transalkylation has been proposed in that the alkyl distribution pattern is the result of rearrangement from one porphyrin molecule to another (Hodgson et al., 1974; Bonnett et al., 1972, 1978). Chlorobium chlorophylls (bacterial chlorophyll) have also been postulated as porphyrin precursors (Barker et al., 1967). Treibs assumptions do not explain the existence of the other types of porphyrins. It has been suggested that Di-DPEP may arise from condensation of the vinyl group of chlorophyll a whereas the rhodoporphyrins arise from condensation of porphyrin side-chains during diagenesis to produce the benzene ring (Figure 45) (Barwise and Whitehead, 1980).

The presence of metal-free porphyrins in the solvent extract of the Kerosene Creek oil shale is unusual. These porphyrins are relatively unstable compared to the metal-complexed porphyrins. Either the porphyrins exist in the demetallated form in the shale or else they are complexed with a labile metal (other than nickel or vanadium) which is subsequently lost during the chromatographic procedure. The latter is more likely. The stable nickel porphyrins were detected in the carbonised oil shale.

No electronic spectra,(visible and near U.V.), were obtained for the porphyrins because of their low concentrations.

(vi) Amides

The aliphatic amide fraction constituted 2% and 6% of the EOM in the Kerosene Creek and the carbonised shales respectively. The Kerosene Creek shale contained

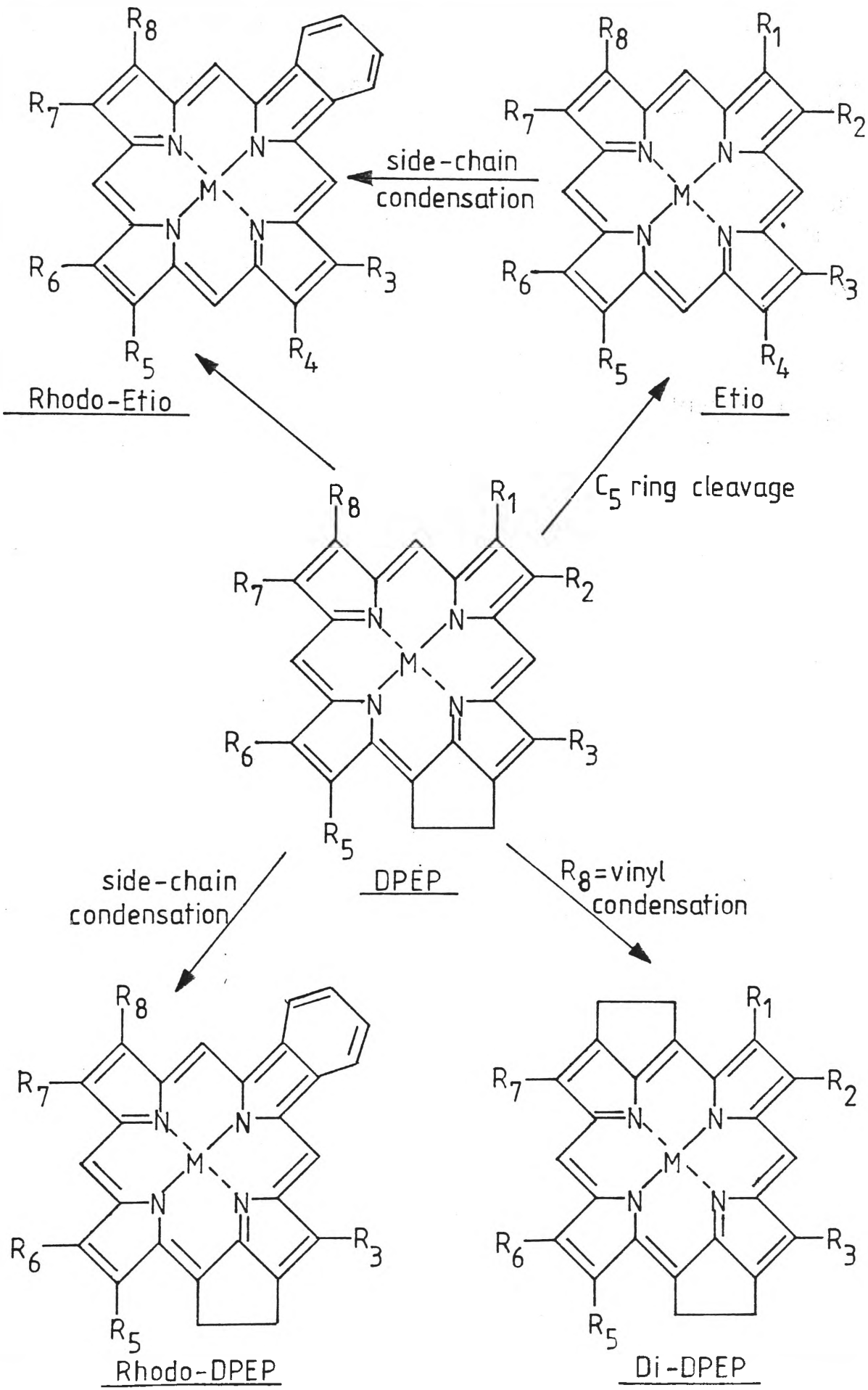


Figure 45. Possible geochemical pathways to the various porphyrins (Barwise and Whitehead, 1980)

saturated aliphatic amides ranging from C_{14} to C_{18} and monounsaturated amides from C_{16} to C_{22} with even carbon number preference (Figure 46). The C_{22}-monounsaturated amide was the most abundant compound and probably has a unique biological source. Saturated aliphatic amides in the carbonised shale range from C_{10} to C_{18} with a maximum at C_{14} and even carbon number prerence whereas the monounsaturated amides range from C_{14} to C_{18} with a maximum at C_{18} and even carbon number preference (Figure 46). The C_{18} monounsaturated amide was the most abundant compound in the carbonised shale. Monounsaturated amides are known metabolites of certain anaerobic bacteria, e.g. Clostridium butyricum (Scheuerbrandt et al., 1961). The presence of aliphatic amides suggests that amide linkages may be important structural elements in the Rundle kerogen.

(vii) Carboxylic acids

The free carboxylic acids present in the solvent extracts of the Kerosene Creek shale and the carbonised shale are shown in Figure 47. They represent 10% and 7% of the EOM in the Kerosene Creek and the carbonised shale respectively (Table 15). Linear saturated carboxylic acids occur in the Kerosene Creek shale ranging from C_6 - C_{30}, local maxima at C_9 and C_{24}, with the C_{28} being the most abundant acid whereas in the carbonised shale they range from C_6 to C_{18} with a maximum at C_{16}. The saturated carboxylic acids in the Kerosene Creek shale showed even carbon number preference in the region C_{12} - C_{28} suggestive of a plant wax origin for the C_{24} - C_{28} acids and of a fat/lipid origin for

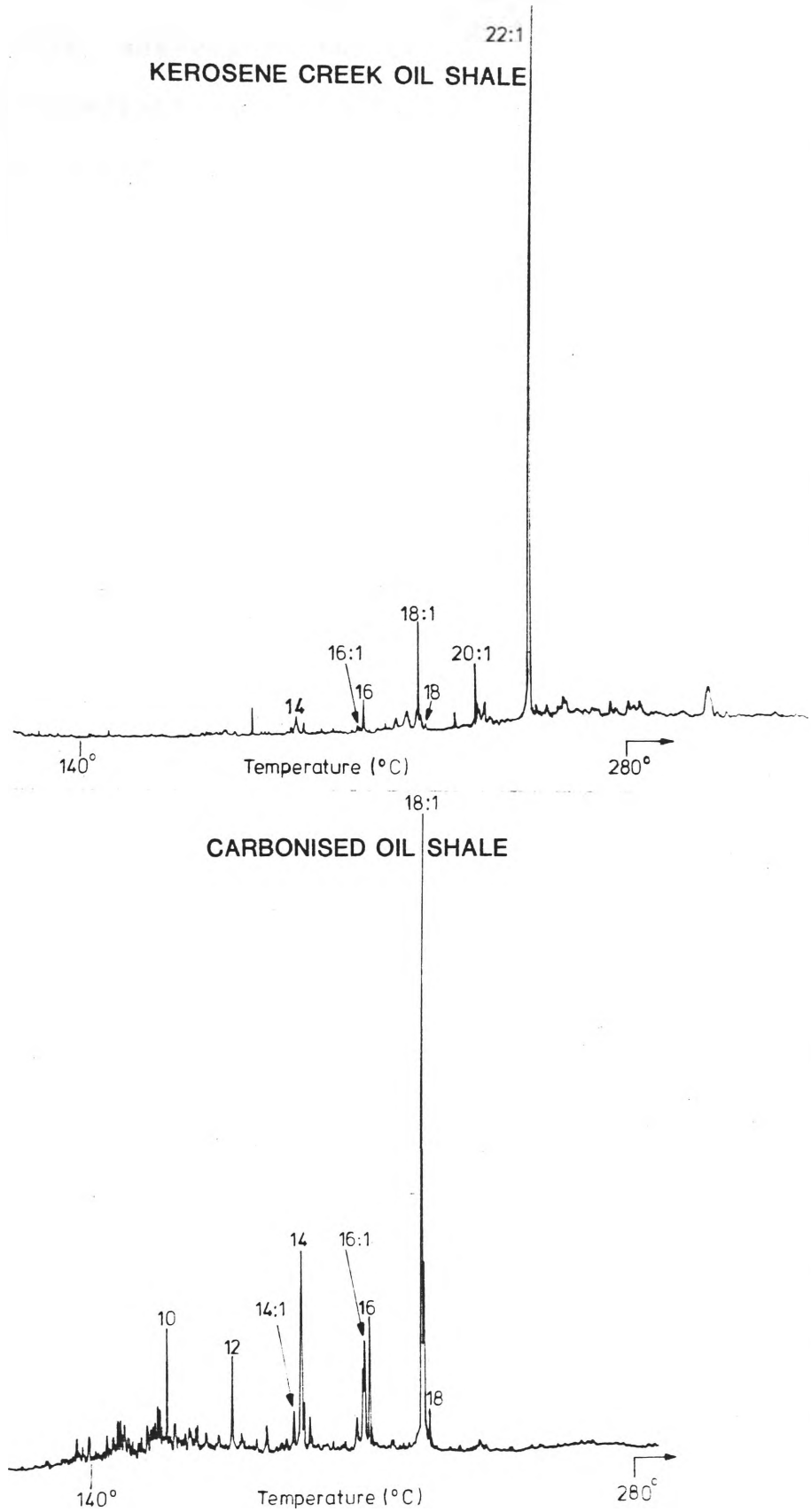


Figure 46. Gas chromatograms of the amide fractions from the solvent extracts of the Kerosene Creek and carbonised oil shales. Carbon numbers of homologous aliphatic amides are indicated. Monounsaturated amides are indicated by e.g. 14:1.

$\leqslant C_{24}$ acids, whereas in the carbonized shale even carbon number preference occurred in the region C_{10} to C_{18}. Normal fatty acids are one likely source of the polymethylene chains which have been shown to be present in kerogen (Gallegos, 1976; Ishiwatari and Machihara, 1982a), and hence of the alkanes liberated by pyrolysis. However, such claims could also originate from linear polymers secreted by algae (similar to Botryococcus; Douglas et al., 1969; Cane and Albion, 1973) or from long-chain alkanes present in plants (Gallegos, 1976).

Homologous α,ω -dicarboxylic acids were also detected in the Kerosene Creek shale (C_9 - C_{22}, maxima C_{14} and C_{20}, no carbon number preference) though in much lower concentrations that the monocarboxylic acids. Dicarboxylic acids have been reported infrequently in solvent extracts of rocks (Haug et al., 1967; Burlingame et al., 1969b). Johns and Onder, (1975) have suggested that they may result from bacterial oxidation of lipids during early diagenesis. No dicarboxylic acids were detected in the carbonised shale. Instead homologous mono-unsaturated acids ranging from C_{14} to C_{18} were detected, with C_{16} and C_{18} being the most abundant. No monounsaturated acids were detected in the Kerosene Creek oil shale. Palmitic (C_{16}) and stearic acid (C_{18}), together with their unsaturated counterparts with the same carbon numbers, are the most abundant fatty acids in lipids from algae and higher plants.

(viii) Polymeric material

Asphaltenes comprised the bulk of the solvent extractable material, with 66% in the Kerosene Creek oil shale and 52% in the carbonised shale. The elemental analysis of the asphaltenes in the Kerosene Creek oil shale is as follows:

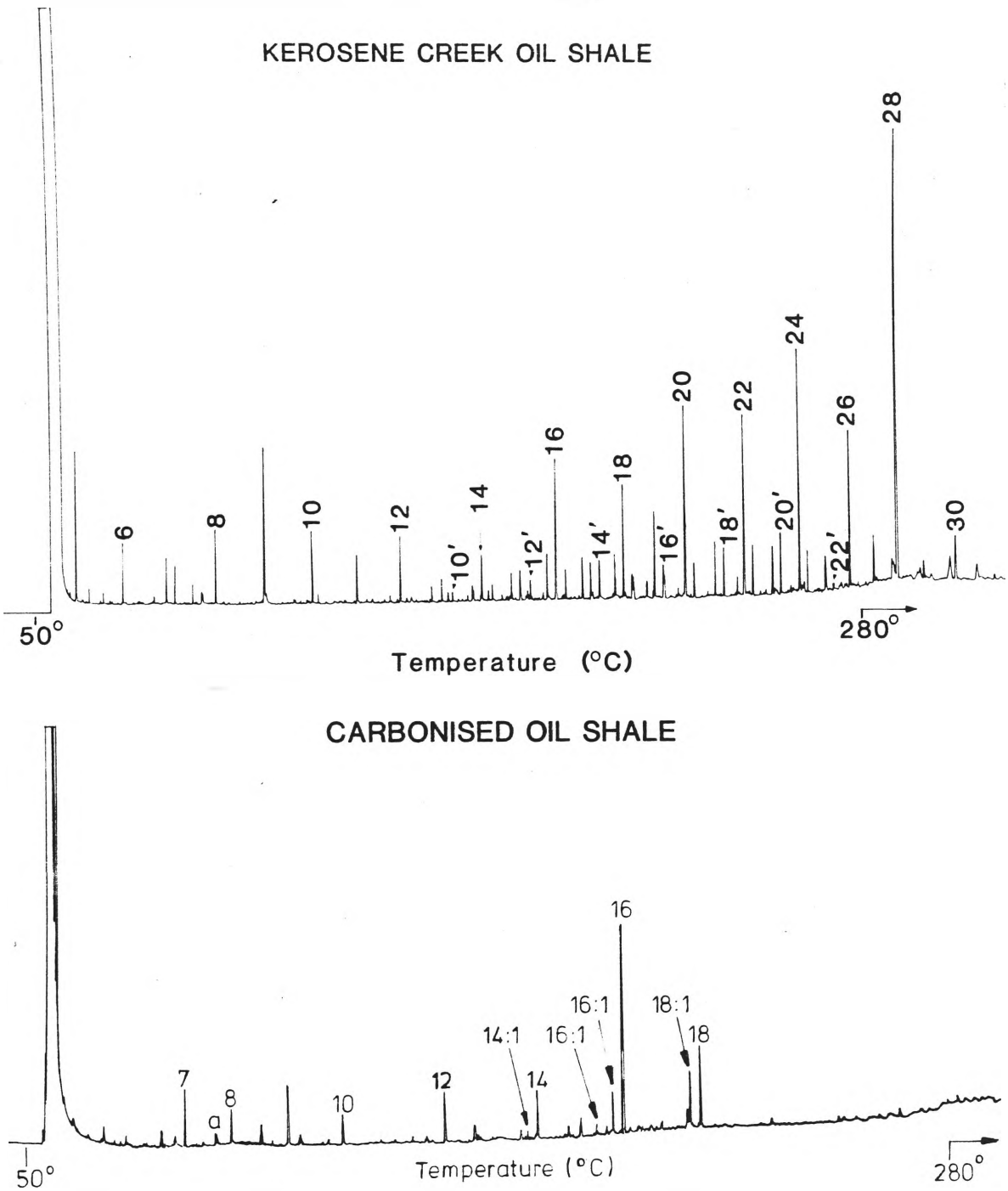


Figure 47. Gas chromatograms of the acid fractions from the solvent extracts of the Kerosene Creek and carbonised oil shales. Carbon numbers are indicated for homologous methylesters of mono-carboxylic acids (no prime) and α,ω -dicarboxylic acids (with prime). Monounsaturated acids in the carbonised oil shale are indicated by e.g. 14:1. a=benzoic acid

70.5% C, 10.2% H, 1.3% N, 12.0% O, 0.6% S, and 4.0% residue. It was found that long straight-chain carboxylic acids adsorbed onto the asphaltenes and therefore the asphaltenes were treated with BF_3/methanol to methylate the acids, which were then combined with the acids extracted by $NaHCO_3$ solution. Long straight-chain acids also adsorbed onto the humic acids which were obtained from the alkaline hydrolysis and potassium permanganate oxidation (following sections). Therefore it was necessary to wash the humic acids with ether to remove the adsorbed acids.

Polymeric material was also obtained from the open-column chromatographic procedure (Table 15).

B) Alkaline hydrolysis

The profile of the carboxylic acids present in the alkaline extract of the Kerosene Creek shale differed markedly from that of the solvent extract. Dicarboxylic acids were now much more abundant than monocarboxylic acids for carbon numbers ≥ 18 (Figure 48). The monocarboxylic acids (C_5 - C_{28}) showed distinct maxima at C_{16} and C_{24} and even carbon number preference. The C_{28} acid was much less abundant that in the solvent extract. The dibasic acids (C_6 - C_{26} ; maxima C_{11}, C_{14}, very large maximum at C_{21}) were now more abundant than the monocarboxylic acids, particularly around C_{21}. Benzoic acid was found in low concentration, but unsaturated acids were not detected.

The carboxylic acids present in the alkaline extract of the carbonised shale are similar to those of the solvent extract, i.e. linear saturated acids, C_6 to C_{18} with a maximum at C_{16} and

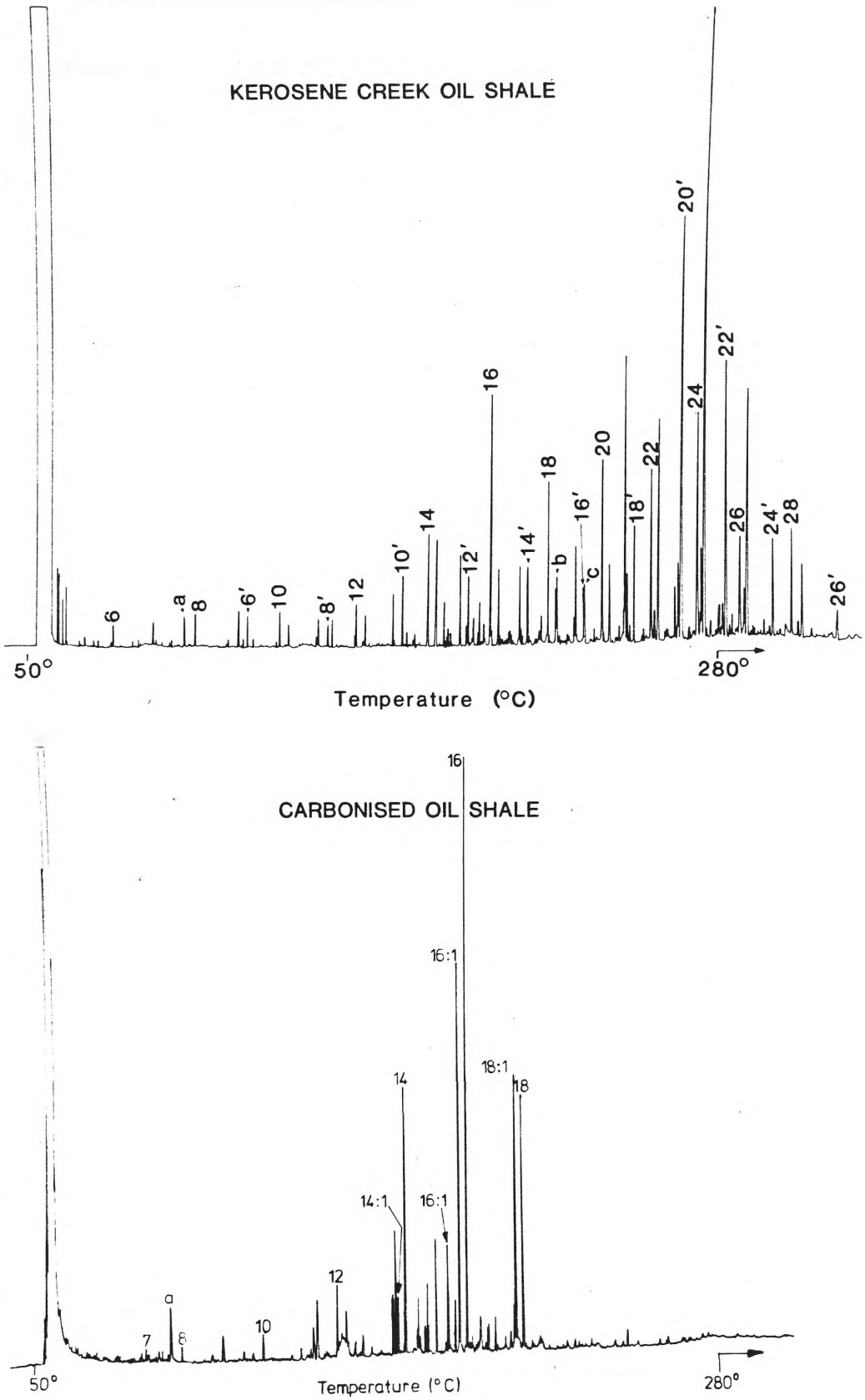


Figure 48. Gas chromatograms of the alkaline methanol extracts from the Kerosene Creek and carbonised oil shales. Carbon numbers are indicated for homologous methyl esters of monocarboxylic acids (no prime) and α,ω -dicarboxylic acids (with prime); a=benzoic acid; b=2-methyloctadecanoic acid; c=2-methylnonadecanoic acid. Monounsaturated acids in the carbonised oil shale are indicated by e.g. 14:1

linear monounsaturated acids, C_{14} to C_{18} (Figure 48). No dicarboxylic acids were detected in the carbonised shale. The concentration of acids in the range C_{14} to C_{18} appears to be greater in the alkaline extract than in the solvent extract. Benzoic acid was detected in low concentration.

The carbon number distribution of the monocarboxylic acids in the Kerosene Creek shale obtained from the alkaline hydrolysis was biased towards the lower carbon numbers whereas that from the solvent extract was biased towards higher carbon numbers. This suggests that the longer chain acids are more readily adsorbed onto the kerogen (possibly as anions at cationic kerogen sites) and less readily bound into the kerogen by the formation of ester linkages (by condensation with hydroxyl functions or by addition to carbon-carbon double bonds). Such partitioning of the original lipids between adsorbed and chemically bound states may have occurred during the early stages of diagenesis.

Alkaline methanol extracted larger amounts of dicarboxylic acids from the Kerosene Creek shale than did benzene/methanol. This is no doubt due to cleavage of ester linkages in the kerogen. The α,ω -dicarboxylic acids could serve to build up a polymeric network in the kerogen by formation of ester linkages at each end of the chain (Djuricic et al., 1971). The low yields of these acids in the Kerosene Creek shale (2% of the organic carbon) suggest that only those diesters at or close to the surface of the shale are accessible to the alkaline reagent. The absence of dicarboxylic acids in the alkaline methanol extract of the carbonised shale would suggest that there are no diesters at or close to the surface. Only 2%

of the organic carbon in the carbonised shale was extracted with alkaline methanol.

The precipitated acids in the Kerosene Creek shale were dark brown in colour and were probably humic acids derived from biodegradation of lignins and tannins present in the terrigenous component of the source material (Reuter and Perdue, 1977). The ratio of precipitated : ether soluble acids was 5:1. The formation of humic substances may be considered a two stage process. In the first stage, plant material is mechanically disintegrated and with the help of microorganisms depolymerised into aromatic, phenolic and carboxylic moieties. In the second stage, the polymers of humic substances are built up by random repolymerisation and polycondensation of the molecular types. There were no humic acids extracted from the carbonised shale. Upon heating, humic substances are converted to kerogen-like material and show a graphite-like structure (Ishiwatari et al., 1977).

C) Alkaline potassium permanganate oxidation

Although the alkaline permanganate oxidation of the Kerosene Creek shale was conducted in seven successive stages, the profiles of the acidic organic products produced at each stage were very similar. The bulk of these products was formed during the first few additions of permanganate, which also showed by far the fastest rates of reaction (Figure 49). These findings suggest that, at the molecular level, the relative extent of oxidation of different structural entities within the kerogen is rather insensitive to the absolute concentration of permanganate and further that, as for the

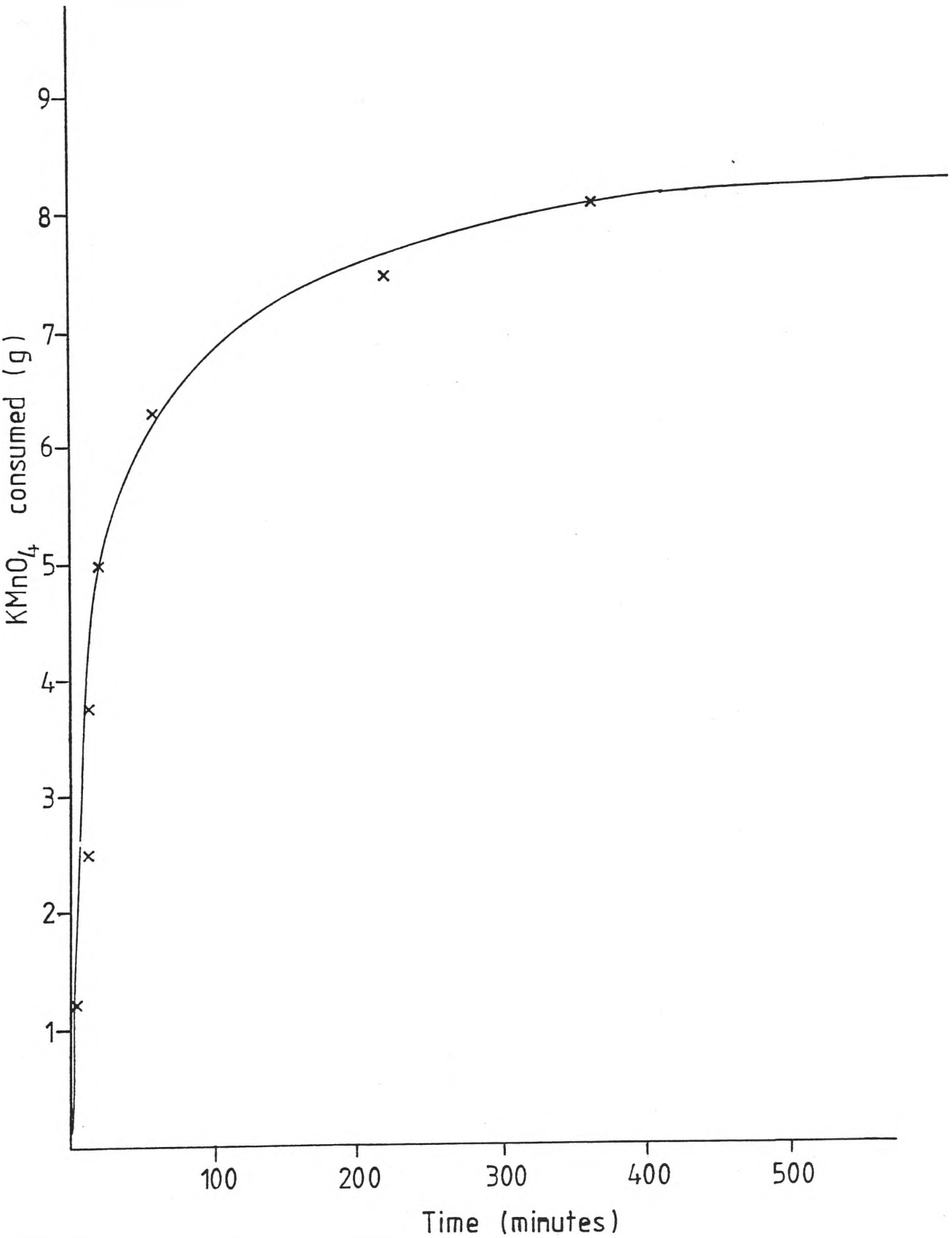


Figure 49. Rate of oxidation for the Kerosene Creek oil shale by alkaline permanganate solution

alkaline hydrolysis, the extent of chemical oxidation is restricted to the organic material at or very near to the surface of the shale particles. The maximum yield of carboxylic acids was found for the fourth addition of permanganate (Figure 50). This suggests that the earlier additions served to render the shale surface more polar and, by dissolution of portions of the organic material, more porous and hence of larger effective surface area. Similar increases in wettability have been observed in coals which have undergone aerial oxidation after exposure to the atmosphere (Van Krevelen, 1981).

The ratio of dicarboxylic acids to monocarboxylic acids in the Kerosene Creek shale was even greater in the alkaline permanganate extract, than in the alkaline methanol extract. The dicarboxylic acids ranged from C_4 to C_{26}, with maxima at C_9 and C_{20} and no carbon number preference (Figure 51). These maxima are two and one carbon less than the respective maxima in the alkaline methanol extract, which is indicative of oxidative degradation of carbon chains by the permanganate. This is further evidenced by: the higher intensity of the C_9 maximum relative to the C_{20} maximum; the reduction of the TOC of the shale from 10.5 to 0.4%; and the fact that the recovered carboxylic acids account for only 58% of the original TOC. The formation of non-recovered oxidation products such as carbon dioxide, water-soluble carboxylic acids (not readily extracted into ether) and volatile carboxylic acids would account for the balance of the TOC. Unlike simple hydrolysis, permanganate has been shown to attack C=C and some activated C-C linkages (March, 1968). A large portion of the α,ω -dicarboxylic acids

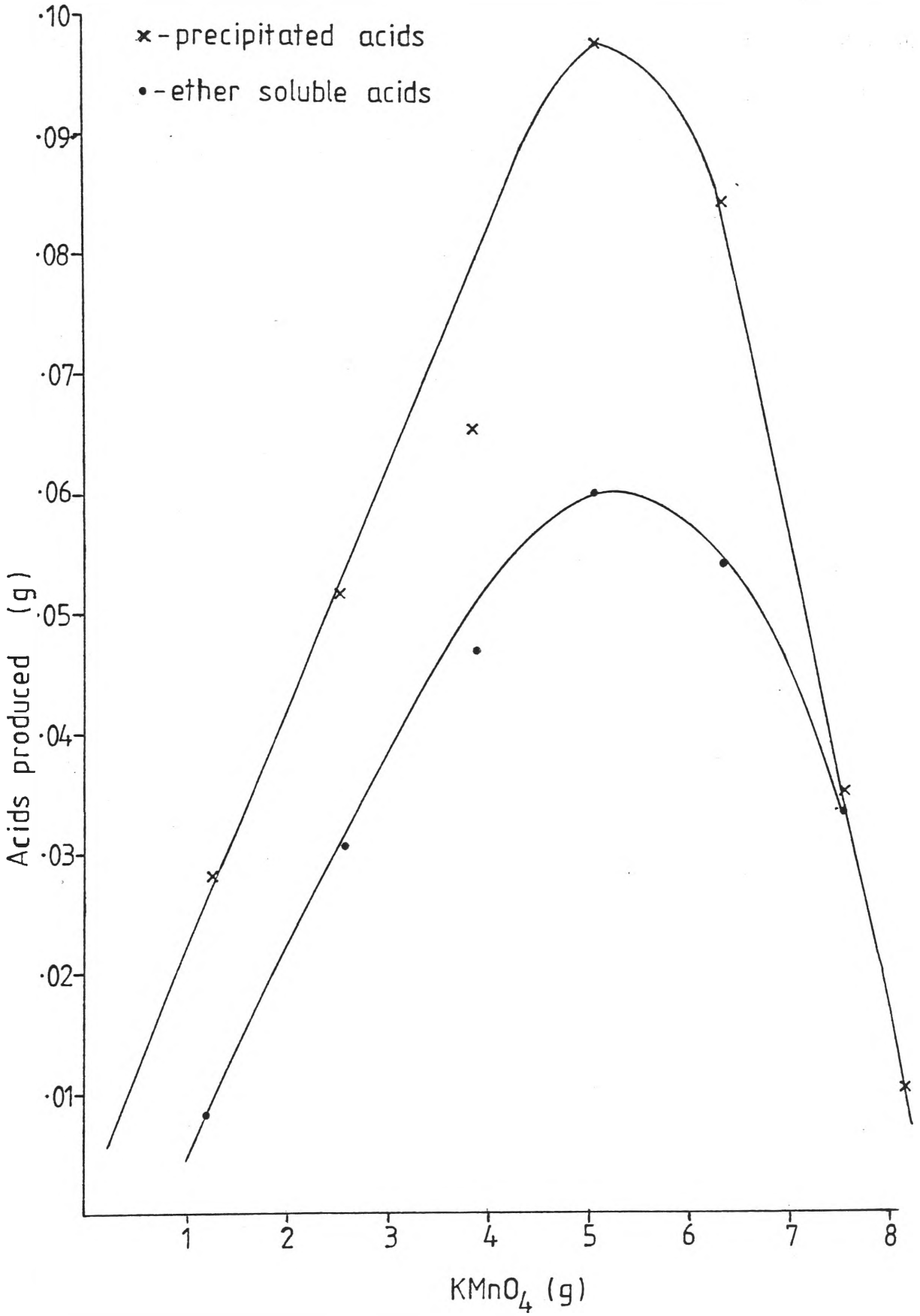


Figure 50. Yields of precipitated and ether soluble acids from the step-wise oxidation of the Kerosene Creek oil shale

may have been derived from unsaturated fatty acids by oxidative cleavage of carbon-carbon double bonds (Van Vleet and Quinn, 1976). The monocarboxylic acids (C_5 - C_{26}, maxima C_6, C_{14}) showed only slight carbon number preference. Small amounts of branched chain monocarboxylic acids were detected amongst the permanganate oxidation products. Trace amounts of benzoic acid, 3,7,11-trimethyldodecanoic acid and 4,8,12-trimethyltridecanoic acid were detected in the Kerosene Creek shale. The ratio of precipitated:ether soluble acids was 1.3. The precipitated (humic) acids are highly aliphatic in character (H/C=1.5).

The specific yield of carboxylic acids from permanganate oxidation of the Kerosene Creek shale was similar to that obtained from the Green River shale (Robinson et al., 1953; Djuricic, 1971). The very low abundance of benzoic acid suggests that the Kerosene Creek shale contains predominantly algal lipid remains. Aromatic carboxylic acids were almost absent in the permanganate extract, in accord with the low abundance of phenylalkanes in the composite Rundle retort oil. The alkaline oxidation is probably in part a simple hydrolysis of ester linkages as well as an oxidative cleavage of C-C bonds in the polymethylene bridges. The main indications of contributions from the latter are the disappearance of carbon number preference in the monocarboxylic acids, and a bias towards lower molecular weights compared with the acids obtained by alkaline methanol extraction of the shale. Straight chain dicarboxylic acids have been produced by oxidative degradation of sporinite (Brooks and Shaw, 1972), cutinite (Hunnaman and Eglinton, 1969), alginite (Simoneit and Burlingame, 1973) and humic acids (Maximov et al.,1972). The carbon number profile of

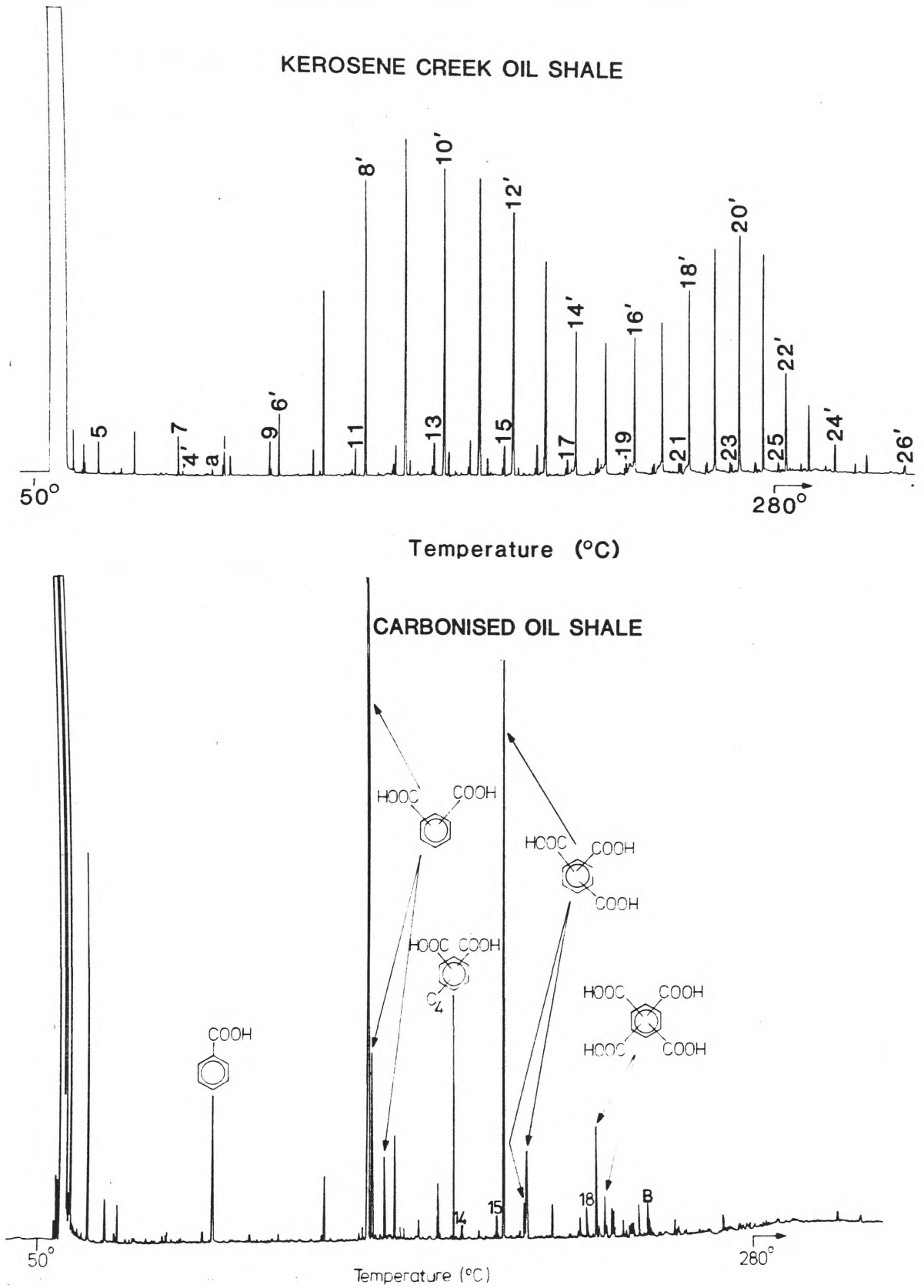


Figure 51. Gas chromatograms of the permanganate oxidation extracts from the Kerosene Creek and carbonised oil shales. Carbon numbers are indicated for homologous methyl esters of monocarboxylic acids (no prime) and α,ω -dicarboxylic acids (with prime); a=benzoic acid.
B=dehydroabietic acid

α,ω -dicarboxylic acids in the Kerosene Creek shale resembled that produced by oxidation of contemporary algal lipids (Ishiwatari and Machihara, 1982a) and also corresponds with the profile of aliphatic hydrocarbons (predominantly C_8 - C_{24}) in the Rundle retort oil.

The oxidation of the carbonised shale was performed in two steps. In the first step, oxidation was completed after 15 minutes whereas in the second step the permanganate was not reduced even after 24 hours. No α,ω-dicarboxylic acids were detected amongst the oxidised products. The first step contained an abundance of aliphatic saturated and mono-unsaturated acids (C_{14} - C_{18}) similar to the alkaline methanol extract, as well as benzoic acid and benzene dicarboxylic acid isomers. The benzene dicarboxylic acid was the dominant compound. One would not expect to obtain monounsaturated acids from a $KMnO_4$ extract. These acids should be converted to mono- and dicarboxylic acids. Presumably they were liberated by the alkali after the $KMnO_4$ had been consumed (by preferential oxidation of alkyl aromatics). The second step contained predominantly benzene carboxylic acids ranging from mono- to tetracarboxylic acids (Figure 51). Only trace amounts of the aliphatic monocarboxylic acids were detected. The second step extracted twice the amount of acids as in the first step. Altogether, the recovered carboxylic acids accounted for only 30% of the original TOC. The permanganate oxidation reduced the TOC of the carbonised shale from 0.5 to 0.1%. The low yields of recoverable acids are probably due to the formation of nonrecovered oxidation products such as CO_2.

The yield of the benzene polycarboxylic acids in the carbonised oil shale is in the following order: benzene dicarboxylic > tricarboxylic > tetracarboxylic acids. This result indicates that aromatic structures with smaller numbers of carbon substitution are formed more easily than those with larger numbers of carbon substitution in kerogen under the thermal conditions. Benzoic acid was also present and is considered to be derived from phenylalanine or its derivatives (Machihara and Ishiwatari, 1980).

It would appear that thermal alteration of the kerogen results in cleavage and release of polymethylene chains and subsequent cyclisation of the polymethylene chain. This results in producing predominantly aromatic acids and a disappearance of the α,ω-dicarboxylic acids upon oxidation of the kerogen. This is consistent with the results obtained by Ishiwatari and Machihara (1982b) who artificially heated kerogen to 400^{o}C and found that the yields of benzene carboxylic acids upon oxidation increased with increasing heat. The kerogen becomes more graphite-like in structure upon increasing thermal alteration (Ishiwatari et al., 1977). No humic acids were extracted upon oxidation of the kerogen.

Dehydroabietic acid was also detected in small quantities in the carbonised shale. This could be derived from abietic acid, a common diterpenoid acid in the resins of higher plants (Simoneit, 1977; Laflame and Hites, 1978).

CONCLUSION

This is the first detailed chemical study of an Australian oil shale, with complementary data on retort oils, solvent extractable materials and chemical degradation products. The shale oils, which were produced by Fischer Assay retorting from the various stratigraphic levels of the Rundle deposit, have similar chemical compositions, but are substantially different to those obtained by pyrolysis in the Lurgi-Ruhrgas process. The composition of the retort oils, solvent extract and the chemical degradation products, indicate a predominantly algal source for the kerogen, although some terrestrial input is evident. The presence of chemically labile and thermally unstable compounds in the solvent extract of the Kerosene Creek oil shale demonstrates the immaturity of the Rundle deposit. These findings are in accord with geological evidence.

There is a need to study the chemical composition of the oil at successive stages of the retorting process, as well as under different retorting conditions. This is evident from the difference in the chemical composition of the oils extracted by the Fischer Assay retort, compared with those from the Lurgi-Ruhrgas process. For this, a microscale pyrolysis technique combined with gas chromatography-mass spectrometry is probably a faster and more convenient technique than the Fischer Assay retort. The nature of the products obtained from the small scale pyrolysis reactions provide a guide to the types of products that can be expected on large scale liquefaction of oil shales.

A detailed knowledge of the constituents of shale oil is

essential for the development of techniques for its subsequent refining and safe handling. The identification of aliphatic and aromatic nitrogen compounds in the oil is significant for the design of catalytic refining processes, since non-basic nitrogen compounds, such as aliphatic nitriles, may not poison acidic catalysts to the same extent as heteroaromatic nitrogen compounds. Therefore, to apply the most effective methods and conditions for the removal of nitrogen compounds, it is important to know the types of nitrogen compounds present in the oil.

Shale oil polymerises on standing to give a viscous product which is difficult to transport. The mechanism by which this process occurs remains to be determined but this study has identified many of the possible components, such as alkenes, nitrogen and oxygen compounds, involved in the polymerisation reactions. The identification of such compounds is important to determine the mechanism(s) of polymerisation so that optimum storage conditions and potential inhibitors may be defined.

Scottish shale oil is known to be carcinogenic to man and it is likely that other shale oils share this property. The Rundle shale oil contains polyaromatic hydrocarbons and many nitrogen compounds; both of these classes contain members which are known or suspected carcinogens. It is hoped that the separation scheme developed for shale oil analyses will permit separation and identification of the toxic constituents of shale oil.

Shale oil has a very different composition to that of petroleum and offers a valuable source of raw materials to

the chemical industry (e.g. alkenes, ketones and nitriles). It is likely that oil shale development will be accelerated if separation and utilization techniques can be devised for these compounds.

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REFERENCES

Allan J., Bjoroy M and Douglas A.G. (1980) A chemical study of the exinite group maceral alginite selected from three Permo-Carboniferous torbanites. In Advances in Organic Geochemistry 1979 (Physics and Chemistry of the Earth Vol. 12) (eds. A.G. Douglas and J.R. Maxwell), p 599-618. Pergamon Press.

Anders D.E. and Robinson W.E. (1971) Cycloalkane constituents of the bitumen from Green River shale. Geochim. Cosmochim. Acta 35, 661-678.

Anders D.E., Doolittle F.G. and Robinson W.E. (1973) Analysis of some aromatic hydrocarbons in a benzene-soluble bitumen from Green River shale. Geochim. Cosmochim. Acta 37, 1213-1228.

Arpino P. and Ourisson G. (1971) Interactions between rock and organic matter. Esterification and transesterification induced in sediments by methanol and ethanol. Anal. Chem. 43, 1656-1657.

Attaway D. and Parker P.L. (1970) Sterols in recent marine sediments. Science 169, 674-676.

Ball L.C. (1914) Tertiary oil shales of The Narrows, Port Curtis District. Qld. Govt. Min. J., 15, 73-76.

Ball L.C. (1946) Oil shales of The Narrows, Central Queensland. Qld. Govt. Min. J. 47, 176-179.

Barker E.W., Yen T.F., Dickie J.P., Rhodes R.E. and Clarke L.F. (1967) Mass spectrometry of porphyrins. II. Characterisation of petroporphyrins. J. Amer. Chem. Soc. 89, 3631-3639.

Barwise A.J.G. and Whitehead E.V. (1980) Separation and structure of petroporphyrins. In Advances in Organic Geochemistry 1979 (Physics and Chemistry of the Earth Vol. 12) (eds. A.G. Douglas and J.R. Maxwell), p 181-192. Pergamon Press.

Bendoraitis J.G., Brown B.L. and Hepner L.S. (1962) Isoprenoid hydrocarbons in petroleum. Anal. Chem. 34, 49-53.

Bird C.W., Lynch J.M., Pirt S.J. and Reid W.W. (1971a) The identification of hop-22(29)-ene in prokaryotic organisms. Tetrahedron Lett. 3189-3190.

Bird C.W., Lynch J.M., Pirt F.J., Reid W.W., Brook C.J.W. and Middleditch B.S. (1971b) Steroids and squalene in Methylococcus capsulatus grown on methane. Nature 230, 473.

Bjorseth A. (1977) Analysis of polycyclic aromatic hydrocarbons in particulate matter by glass capillary gas chromatography. Anal. Chim. Acta 44, 21-27.

Blumer M., Mullin M.M. and Thomas D.W. (1964) Pristane in the marine environment. Helgolaender Wiss. Meeresuntersuch 10, 187.

Blumer M., Guillard R.R.L. and Chase T. (1971) Hydrocarbons of marine phytoplankton. Mar. Biol. 8, 183-189.

Blunt J.W., Hartshorn M.P. and Kirk D.N. (1969) Reactions of epoxides. XVII. Backbone rearrangements of cholest-5-ene and 5,6α-epoxy-5α-cholestane. Tetrahedron 25, 149-153.

Bonnett R., Brewer P., Noro K. and Noro T. (1972) On the origin of petroporphyrin homologues: the transalkylation of vanadyloctaalkylporphyrins. Chem. Commun. 562-563.

Bonnett R., Brewer P., Noro K. and Noro T. (1978) Chemistry of vanadylporphyrins. Tetrahedron 34, 379-385.

Brooks J. and Shaw G. (1972) Geochemistry of sporopollenin. Chem. Geol. 10, 69-87.

Brown S., Bailie T.A. and Burlingame A.L. (1980) Analytical approaches to the investigation of kerogen structure by mass spectrometric techniques. In Advances in Organic Geochemistry 1979 (Physics and Chemistry of the Earth Vol. 12) (eds. A.G. Douglas and J.R. Maxwell), p 475-484. Pergamon Press.

Brown F.R. and Karn F.S. (1980) Stability studies of coal-derived liquids. Fuel 59, 431-435.

Burlingame A.L. and Simoneit B.R. (1968) Isoprenoid fatty acids isolated from the kerogen matrix of the Green River formation (Eocene). Science 160, 531-533.

Burlingame A.L., Haug P.A., Schnoes H.K. and Simoneit B.R. (1969a) Fatty acids derived from the Green River formation oil shale by extractions and oxidations. A Review. In Advances in Organic Geochemistry 1968 (eds. Schenck P. B. and I. Havenaar), p 85-129. Pergamon Press.

Burlingame A.L., Wszolek P.C. and Simoneit B.R. (1969b) The fatty acid content of Tasmanites. In Advances in Organic Geochemistry 1968 (eds. P.A.Schenck and I. Havenaar), p 131-154. Pergamon Press.

Burnham A.K., Clarkson J.E., Singleton M.F., Wong C.M. and Crawford R.W. (1982) Biological markers from Green River kerogen decomposition. Geochim. Cosmochim. Acta 46, 1243-1251.

Cane R.F. (1967) The constitution and synthesis of oil shale. Proc. 7th World Pet. Congr., III 681-689, Elsevier.

Cane R.F. and Albion P.R. (1971) The Phytochemical history of Torbanites. J. Proc. Royal Soc. N.S.W. 104, 31-37.

Cane R.F. and Albion P.R. (1973) Organic geochemistry of torbanite precursors. Geochim. Cosmochim. Acta 37, 1543-1550.

Chmielowiec J. and George A.E. (1980) Polar bonded-phase sorbents for high performance liquid chromatographic separations of polycyclic aromatic hydrocarbons. Anal. Chem. 52, 1154-1157.

Clark B.R., Ho C.H. and Jones A.R. (1975) Adv. Chem. Ser. 170, 282-294.

Corbet B., Albrecht P. Ourisson G. (1980) Photochemical or photomimetic fossil triterpenoids in sediments and petroleum. J. Amer. Chem. Soc. 102, 1171-1173.

Cox R.E., Maxwell J.R., Ackman R.G. and Hooper S.N. (1972) The isolation of a series of acyclic isoprenoid alcohols from an ancient sediment: approaches to a study of the diagenesis and maturation of phytol. In Advances in Organic Geochemistry (eds. H.R. von Gaertner and H. Wehner), p 263-276. Pergamon Press.

Dark W.A. and McFadden W.H. (1978) The role of HPLC and LC-MS in the separation and characterization of coal liquefaction products. J. Chromatogr. Sci. 16, 289-293.

Dark W.A. and McGough R.R. (1978) Use of liquid chromatography in the characterization of asphalts. J. Chromatogr. Sci. 16, 610-615.

Davis J. (1967) Petroleum Microbiology p 299, Elsevier.

Day W.C. and Erdman J.G. (1963) Ionene: a thermal degradation product of β-carotene. Science 141, 982-984.

DePuy C.H. and King R.W. (1960) Pyrolytic cis eliminations Chem. Rev. 60, 431-457.

DeRosa M. Gambacorta A., Minale L. and Bu'Lock J.D. (1971) Bacterial triterpenes. Chem. Commun. 620

Didyk B.M., Simoneit B.R.T., Brassell S.C. and Eglinton G. (1978) Organic geochemical indicators of palaeo-environmental conditions of sedimentation. Nature 272, 216-222.

Diekman J. and Djerassi C. (1967) Mass spectrometry in structural and stereochemical problems: Mass spectrometry of some steroid TMS. J. Org. Chem. 32, 1005.

Dinneen G.U., Smith J.R., Van Meter R.A., Allbright C.S. and Anthoney W.R. (1955) Application of separation techniques to a high boiling shale oil distillate. Anal. Chem. 27, 185-190.

DiSanzo F.P., Uden P.C. and Siggia S. (1980) Shale oil hydrocarbon separation by preparative liquid chromatography and glass capillary gas chromatography. Anal. Chem. 52, 906-909.

Djuricic M., Murphy R.C., Vitorovic D and Biemann K. (1971) Organic acids obtained by alkaline permanganate oxidation of kerogen from the Green River shale. Geochim. Cosmochim. Acta 35, 1201-1207.

Douglas A.G., Douraghi-Zadeh K. and Eglinton G. (1969) The fatty acids of the alga Botyrococcus braunii. Phytochemistry 8, 285-293.

Eglinton G. and Hamilton R.J. (1963) The distribution of alkanes. In Chemical Taxonomy (ed T. Swain), p 187-217, Academic Press.

Eglinton G. and Hamilton R.J. (1967) Leaf epicutical waxes. Science 156, 1322-1335.

Ekstrom A. (personal communication) CSIRO Division of Energy Chemistry, Lucas Heights, Australia.

Ensminger A., Albrecht P., Ourisson G., Kimble B.J., Maxwell J.R. and Eglinton G. (1972) Homohopane in Messel oil shale: First identification of a C_{31} pentacyclic triterpane in nature. Tetrahedron Lett. 36, 3861-3864.

Ensminger A., Van Dorsselaer A., Spyckerelle C., Albrecht P. and Ourisson G. (1974) Pentacyclic triterpanes of the hopane type as ubiquitous geochemical markers: origin and significance. In Advances in Organic Geochemistry 1973 (eds. B. Tissot and F. Bienner), p 245-260. Technip.

Evans E.D., Kenny G.S., Meinschein W.G. and Bray E.E. (1957) Distribution of n-paraffins and separation of saturated hydrocarbons from Recent marine sediments. Anal. Chem. 29, 1858-1861.

Finar I.L. (1967) Organic Chemistry. Vol 1, 5th edn., p 323, Longmans.

Ford C.D., Holmes S.A., Thompson L.F. and Latham D.R. (1981) Separation of nitrogen compound types from hydrotreated shale oil products by adsorption chromatography on basic and neutral alumina. Anal. Chem. 53, 831-836.

Forster H., Biemann K., Haugh W.G., Tattrie N.H. and Coluin J.R. (1973) The structure of novel C_{35} pentacyclic terpenes from Acetobacter xylinum. J. Biochem. 135, 133-143.

Gallegos E.J. (1971) Identification of new steranes, terpanes and branched paraffins in Green River shale by combined capillary gas chromatography and mass spectrometry. Anal. Chem. 43, 1151-1160.

Gallegos E.J. (1973) Identification of phenylcycloparaffin alkanes and other monoaromatics in Green River shale by gas chromatography-mass spectrometry. Anal. Chem. 45, 1399-1402.

Gallegos E.J. (1976) Biological fossil hydrocarbons. In Developments in Petroleum Science, 5. Oil shale (eds. T.F. Yen and G.V. Chilingarian), p 149-180. Elsevier.

Gaskell S.J. and Eglinton G. (1975) Rapid hydrogenation of sterols in a contemporary lacustrine sediments. Nature 254, 209-211.

Gaskell S.J. and Eglinton G. (1976) Sterols of a contemporary lacustrine sediment. Geochim. Cosmochim. Acta 40, 1221-1228.

Gearing J.N., Gearing P.J., Lytle T.F. and Lytle J.S. (1978) Comparison of thin-layer and column chromatography for separation of sedimentary hydrocarbons. Anal. Chem. 50, 1833-1836.

Gottschalk G. (1979) Bacterial Metabolism. Springer Verlag.

Greiner A.C., Spyckerelle C. and Albrecht P. (1976) Aromatic hydrocarbons from geological sources. I. New naturally occurring phenanthrenes and chrysene derivatives. Tetrahedron 32, 257-260.

Greiner A.C., Spyckerelle C., Albrecht P. and Ourisson G. (1977) Aromatic hydrocarbons from geological sources. V. Mono- and diaromatic derivatives of hopane. J. Chem. Res. (M), 1977, 3829-3871; (S), 1977, 334.

Grizzle P.L. and Thomson J.S. (1982) Liquid chromatographic separation of aromatic hydrocarbons with chemically bonded (2,4-dinitroanilinopropyl) silica. Anal. Chem. 54, 1071-1078.

Hamway P., Cefola M. and Nagy B. (1962) Factors affecting the chromatographic analysis of asphaltic petroleum and of Recent marine sediment organic matter. Anal. Chem. 34, 43-48.

Han J and Calvin M. (1969) Hydrocarbon distribution of algae and bacteria and microbial activity in sediments. Proc. Natl. Acad. Sci. U.S.A. 64, 436-443.

Hanson R.L. and Vanderborgh N.E., Brookins D.G. (1975) Characterization of oil shales by laser pyrolysis-gas chromatography. Anal. Chem. 47, 335-338.

Hartung G.K. and Jewell D.M. (1962a) Identification of nitriles in petroleum products. Complex formation as a method of isolation. Anal. Chim. Acta 27, 219-232.

Hartung G.K. and Jewell D.M. (1962b) Carbazoles, phenazines and dibenzofuran in petroleum products; Methods of isolation, separation and determination. Anal. Chim. Acta 26, 514-527.

Haug P., Schnoes H.K. and Burlingame A.L. (1967) Isoprenoid and dicarboxylic acids isolated from Colorado Green River shale (Eocene). Science 158, 772-773.

Henderson B.W., Reed W. E., Steel G. and Calvin M. (1971) Isolation and identification of sterols from a Pleistocene sediment. Nature 231, 308-310.

Henderson B.W. and Steel G. (1971) Isolation and characterisation of a triterpenoid alcohol from the Green River shale. Chem. Commun. 1331.

Henstridge D.A. and Missen D.D. (1981) The geology of The Narrows Graben near Gladstone, Queensland, Australia. 51st ANZAAS Congress, Brisbane, Australia.

Hertz H.S., Brown J.M., Chesler S.N., Guenther F.R., Hilpert L.R., May W.E., Paris R.M. and Wise S.A. (1980) Determination of individual organic compounds in shale oil. Anal. Chem. 52, 1650-1657.

Ho C.H., Clark B.R., Guerin M.R., Ma C.Y. and Rao T.K. (1979) Aromatic nitrogen compounds in fossil fuels: a potential hazard. Am. Chem. Soc. Div. of Fuel Chem. 24, 281-291.

Hodgson G.W., Hitchon B., Taguchi K., Baker B.L. and Peake E. (1968) Geochemistry of porphyrins, chlorins and polycyclic aromatics in soils, sediments and sedimentary rocks. Geochim. Cosmochim. Acta 32, 737-772.

Hodgson G.W. and Casagrande D.J. (1974) Generation of homologous porphyrins under simulated geological conditions. Geochim. Cosmochim. Acta 38, 1745-1758.

Hunnaman D.H. and Eglinton G. (1969) Gas chromatographic-mass spectrometric identification of long chain hydroxy acids in plants and sediments. In Advances in Organic Geochemistry 1968 (eds. P.A. Schenck and I. Havenaar), p 157-166. Pergamon Press.

Hutton A.C., Kantsler A.J., Cook A.C. and McKirdy D.M. (1980) Organic matter in oil shales. APEA J. 20, 44-66.

Hutton A.C. (1981) Classification of Australian oil shales. 51st ANZAAS Congress, Brisbane, Australia.

Hutton A.C. (1983) Organic petrology of oil shale. Ph. D. disseration, Univ. of Wollongong.

Iida T., Yoshii E. and Kitatsuji E. (1966) Identification of normal paraffins, olefins, ketones and nitriles from Colorado shale oil. Anal. Chem. 39, 1224-1227.

Ikan R., Baedecker M.J. and Kaplan I.R.(1975a) Thermal alteration experiments on organic matter in recent marine sediments. II. Isoprenoids. Geochim. Cosmochim. Acta 39, 187-194.

Ikan R., Aizenshtat Z., Baedecker M.J. and Kaplan I.R.(1975b) Thermal alteration experiments on organic matter in recent marine sediments. I. Pigments. Geochim. Cosmochim. Acta 39, 173-185.

Ingram L.L., Ellis J., Crisp P.T. and Cook A.C.(1983) Comparative study of oil shale and shale oils from the Mahagony Zone, Green River Formation (U.S.A.) and Kerosene Creek seam, Rundle Formation (Australia). Chem. Geol. 38, 185-212.

Ishiwatari R., Ishiwatari M., Rohrback B.G. and Kaplan I.R. (1977) Thermal alteration experiments on organic matter from recent marine sediments in relation to petroleum genesis. Geochim. Cosmochim. Acta 41, 815-828.

Ishiwatari R. and Machihara T. (1982a) Algal lipids as a possible contributor to the polymethylene chains in kerogen. Geochim. Cosmochim. Acta 46, 1459-1464.

Ishiwatari R. and Machihara T. (1982b) Structural changes of young kerogen during laboratory heating as revealed by alkaline potassium permanganate oxidation. Geochim. Cosmochim. Acta 46, 825-831.

Jackson L.P., Allbright C.S. and Jensen H.B. (1974) Semi-micro procedure for the determination of hydrocarbon types in shale oil distillates. Anal. Chem. 46, 604-606.

Jensen L.S. (1962) The constitution of some bacterial carotenoids and their bearing on biosynthetic problems. KGI Norske Vidensk. Selsk. Skr. 8.

Jensen H.B., Morandi J.R. and Cook C.L. (1968) Abstracts of Papers 155th National Meeting of the American Chemical Society, San Francisco, California. F 98.

Jewell D.M., Ruberto R.G. and Davis B.E. (1972) Systematic approach to the study of aromatic hydrocarbons in heavy distillates and residues by elution adsorption chromatography. Anal. Chem. 44, 2319-2321.

Johns R.B. and Onder D.M. (1975) Biological diagenesis: dicarboxylic acids in Recent sediments. Geochim. Cosmochim. Acta 39, 129-136.

Jones A.R. Guerin M.R. and Clark B.R. (1977) Preparative-scale liquid chromatographic fractionation of crude oils derived from coal and shale. Anal. Chem. 49, 1766-1771.

Jones D.W., Pakdel H. and Bartle K.D. (1982) Cyclic alkanes as geochemical markers in coal liquefaction products. Fuel 61, 44-51.

Kimble B.J., Maxwell J.R., Philp R.P. and Eglinton G. (1974a) Identification of steranes and triterpanes in geolipid extracts by high resolution gas chromatography and mass spectrometry. Chem. Geol. 14, 173-198.

Kimble B.J., Maxwell J.R., Philp R.P. and Eglinton G. (1974b) Tri- and tetraterpenoid hydrocarbons in the Messel oil shale. Geochim. Cosmochim. Acta 38, 1165-1181.

Kirk D.N. and Shaw P.M. (1970) The cholestane backbone rearrangement: Isomerisation at C_{20}. Chem. Commun. 806.

Kollattukudy P.E. (1971) Plant waxes. Lipids 5, 259-275.

Laflame R.E. and Hites R.A. (1978) The global distribution of polycyclic aromatic hydrocarbons in Recent sediments. Geochim. Cosmochim. Acta 42, 289-303.

Laflame R.E. and Hites R.A. (1979) Tetra and pentacyclic naturally occurring aromatic hydrocarbons in Recent sediments. Geochim. Cosmochim. Acta 43, 1687-1691.

Later D.W., Lee M.L., Bartle K.D., Kong R.C. and Vassilaros D.L. (1981) Chemical class separation and characterization of organic compounds in synthetic fuels. Anal. Chem. 53, 1612-1620.

Leythaeuser D., Altebaumer F.J. and Schaeffer R.G. (1980) Effect of an igneous intrusion on maturation of organic matter in Lower Jurassic Shales from NW-Germany. In Advances in Organic Geochemistry 1979 (Physics and Chemistry of the Earth Vol. 12) (eds. A.G. Douglas and J.R. Maxwell), p 133-139, Pergamon Press.

Lindner A.W. and Dixon D.A. (1976) Some aspects of the geology of the Rundle oil shale deposit, Queensland. APEA. J. 165-172.

Machihara T. and Ishiwatari R. (1980) Characterization of young kerogen in a lacustrine sediment by alkaline potassium permanganate oxidation. J. Geochem. 14, 279-288.

Mapstone G.E. (1951) In Oil Shale and Cannel Coal (ed. G. Sell) Vol. 2, p 787.

Marciel G.E., Bartuska V.J. and Miknis F.P. (1978) Correlation between oil yields of oil shales and ^{13}C nuclear magnetic resonance spectra. Fuel 57, 505-506.

Marciel G.E., Bartuska V.J. and Miknis F.P. (1979) Improvements in correlation between oil yields of oil shale and ^{13}C nuclear magnetic resonance spectra. Fuel 58, 155-156.

March J. (1968) Advanced organic chemistry: Reactions, mechanism and structure. McGraw-Hill.

Mattern G., Albrecht P. and Ourisson G. (1970) 4-Methyl-sterols and sterols in Messel shale (Eocene). Chem. Commun. 1570-1571.

Maximov O.B., Schapovalov V.E. and Schvets T.V. (1972) Alkaline permanganate oxidation of methylated humic acids. Fuel 51, 185-189.

Maxwell J.R., Cox R.E., Eglinton G. and Pillinger C.T. (1973) Stereochemical studies of acyclic isoprenoid compounds. II. The role of chlorophyll in the derivation of isoprenoid type acids in a lacustrine sediments. Geochim. Cosmochim. Acta 37, 297-313.

McCarthy E.D. and Calvin M. (1967) The isolation and identification of the C_{17} saturated isoprenoid hydrocarbon 2,6,10-trimethyltetradecane from a Devonian shale: The role of squalane as a possible precursor. Tetrahedron 23, 2609-2619.

Mills G.A., Baedekker E.R. and Oblad A.G. (1950) Chemical characterization of catalysts. I. Poisoning of cracking catalysts by nitrogen compounds and potassium ion. J. Amer. Chem. Soc. 72, 1554-1560.

Mourey R.H., Siggia S., Uden P.C. and Crowley R.J. (1980) High performance liquid chromatographic separation of polycyclic aromatic hydrocarbons on microparticulate pyrrolidone and application to the analysis of oil shale. Anal. Chem. 52, 885-891.

Murphy M.T.J., McCormick A. and Eglinton G., (1967) Perhydro-β-carotene in the Green River shale. Science 157, 1040-1041.

Nagy B., Hamway P., Gagnon G.C. and Cefola M. (1960) Separation of n-octadecane-1-C^{14} from asphaltic mixtures by elution chromatography. Geochim. Cosmochim. Acta 21, 151-155.

Nishimoto K., Ito M. and Natori S. (1968) The structures of arundrin, cyclindrin and fernenol: Triterpenoids of fernane and arborane groups of Imperata cylindrica Var. Koenighii. Tetrahedron 24, 735-752.

Nishimura M. (1978) Geochemical characteristics of the high reduction zone of stenols in Suwa sediments and environmental factors controlling the conversion of stenols into stanols. Geochim. Cosmochim. Acta 42, 349-357.

Novotny M., Lee M.L. and Bartle K.D. (1974) The methods for fractionation, analytical separation and identification of polynuclear aromatic hydrocarbons in complex mixtures. J. Chromatogr. Sci. 12, 606-612.

Novotny M., Kump R., Merli F. and Todd L.J. (1980) Capillary gas chromatography-mass spectrometric determination of nitrogen aromatic compounds in complex mixtures. Anal. Chem. 52, 401-406.

O'Leary W.M. (1970) Lipid Metabolisms. In Comprehensive Biochemistry (eds. M. Horkin and E.H. Stotz) Vol. 18, p 246, Elsevier.

Oro J., Tornabene T.G., Nooner D.W. and Gelpi E. (1967) Aliphatic hydrocarbons and fatty acids in some marine and freshwater microorganisms. J. Bacteriol. 93, 1811-1818.

Parker P.L. (1969) Fatty acids and alcohols. In Organic Geochemistry (eds. G. Eglinton and M.T.J. Murphy) p 357-373. Springer-Verlag.

Philp R.P. (1980) Comparative organic geochemical studies of recent algal mats and sediments of algal origin. In Biogeochemistry of Ancient and Modern Environments (eds. P.A. Trudinger, M.R. Walter and B.J. Ralph) p 173-187, Australian Academy of Science , Canberra.

Philp R.P. and Gilbert T.D. (1980) Application of computerised gas chromatography-mass spectroscopy to oil exploration in Australia. APEA J. 20, 221-228.

Philp R.P., Gilbert T.D. and Friedrich J. (1981) Bicyclic sesquiterpenoids and diterpenoids in Australian crude oils. Geochim. Cosmochim. Acta 45, 1173-1180.

Popl M, Dolansky V. and Mostecky J. (1976) Influence of the molecular structure of aromatic hydrocarbons on their adsorptivity on silica gel. J. Chromatogr. 117, 117-127.

Poulson R.E., Jensen H.B., Duvall J.J., Harris F.L. and Morandi J.R. (1972) Determination of compound types in complex mixture using subtraction and gas chromatographic readout. Anal. Instrum. 10, 193-201.

Pym J.G., Ray J.E., Smith G.W. and Whitehead E.V. (1975) Petroleum triterpane fingerprinting of crude oils. Anal. Chem. 47, 1617-1622.

Rajeshwar K., Jones D.B. and DuBow J.B. (1981) Characterization of oil shales by differential scanning calorimetry. Anal. Chem. 53, 121-122.

Reed P.R.Jr. and Warren P.L. (1974) Colorado School of Mines, 69, 221.

Regtop R.A., Crisp P.T. and Ellis J. (1982) Chemical characterization of shale oil from Rundle, Queensland. Fuel 61, 185-192.

Regtop R.A., Ellis J. and Crisp P.T. (1983) Extractable components of oil shale from Rundle, Queensland: Origin and maturation of the kerogen. Proc. 1st Australian workshop on oil shale, Lucas Heights. p 73.

Reich L. and Strivala S.S. (1969) Autoxidation of Hydrocarbons and Polyolefins. p 527, Marcel Dekker, Inc., New York.

Resing H.A., Garroway A.N. and Hazlett R.N. (1978) Determination of aromatic hydrocarbon fraction in oil shale by ^{13}C NMR with magic angle spinning. Fuel 57, 450-454.

Reuter J.H. and Perdue E.M. (1977) Importance of heavy metal-organic matter interactions in natural waters. Geochim. Cosmochim. Acta 41, 325 - 334.

Rhead M.M., Eglinton G. and Draffan G.H. (1971) Hydrocarbons produced by the thermal alteration of cholesterol under conditions simulating the maturation of sediments. Chem. Geol. 8, 277-297.

Robinson W.E., Heady H.H. and Hubbard A.B. (1953) Alkaline permanganate oxidation of oil shale kerogen. Ind. Eng. Chem. 45, 788-791.

Robinson W.E., Cummins J.J. and Stanfield K.E. (1956) Constitution of organic acids prepared from Colorado oil shale based on n-butylesters. Ind. Eng. Chem. 48, 1134-1138.

Robinson W.E. and Lawlor D.L. (1961) Constitution of hydrocarbonlike materials derived from kerogen oxidation products. Fuel 40, 375-388.

Robinson W.E., Lawlor D.L., Cummins J.J. and Fester J.I. (1963) Oxidation of Colorado oil shale. Bureau of Mines, Rept. of Invest. 6166, 33.

Robinson W.E. (1969) Isolation procedures for kerogens and associated soluble organic materials. In Organic Geochemistry. Methods and Results (eds. G. Eglinton and M.T.J. Murphy), p 181-195. Springer-Verlag.

Rohmer M. (1975) Triterpenoides de procaryotes. Ph. D. These, l'Universite Louis Pasteur de Strasbourg, France.

Rohmer M. and Ourisson G. (1976)

a) Structure des Bacteriohopanetétrols d'Acetobacter xylinum.

b) Derives du Bacteriohopane: Variations structurales et répartition.

c) Methyl-hopanes d'Acetobacter xylinum et d'Acetobacter rancens: Une nouvelle famille de composés triterpéniques. Tetrahedron Lett. 40, 3633-3644.

Rosenfeld R.S. and Hellman L. (1971) Reduction and esterification of cholesterol and sitosterol by homogenates of feces. J. Lipid Res. 12, 192-197.

Rouxhet P.G. and Robin P.L. (1978) Infrared study of the evolution of kerogens of different origins during catagenesis and pyrolysis. Fuel 57, 533-540.

Rovere C.R., Crisp P.T., Ellis J. and Bolton P.D. (1983) Chemical characterization of shale oil from Condor, Queensland. Fuel in press.

Rubin I.B., Guerin M.R., Hardigree A.A. and Epler J.L. (1976) Environ. Res. 12, 358-385.

Rubinstein I., Sieskind O. and Albrecht P. (1975) Rearranged sterenes in a shale: Occurrence and simulated formation. J. Chem. Soc. Perkin. Trans. 1. 1833-1835.

Sautoni J.C., Garber H.R. and Davis B.E. (1975) Hydrocarbon group types in gasoline range materials by HPLC. J. Chromatogr. Sci. 13, 367-371.

Sautoni J.C. and Swab R.E. (1975) Rapid hydrocarbon group type analysis by HPLC. J. Chromatogr. Sci. 13, 361-366.

Sautoni J.C. and Garber H.E. (1976) Hydrocarbon group type analysis of petroleum fractions (b.p. 190°-360°C) by HPLC. J. Chromatogr. Sci. 14, 546-548.

Sautoni J.C. and Swab R.E. (1976) Preparative hydrocarbon compound type analysis by HPLC. J. Chromatogr. Sci. 14, 535-537.

Saxby J.D. (1970) Isolation of kerogen in sediments by chemical methods. Chem. Geol. 6, 173-184.

Scheuerbrandt G., Goldfine H., Baronowsky P.E. and Bloch K. (1961) A novel mechanism for the biosynthesis of unsaturated fatty acids. J. Biol. Chem. 236, PC70.

Schiller J.E. and Mathiason D.R. (1977) Separation method for coal-derived solids and heavy liquids. Anal. Chem. 49, 1225-1228.

Schultz R.V., Jorgenson J.W., Maskarinec M.P., Novotny M. and Todd L.J. (1979) Characterization of polynuclear aromatic and aliphatic hydrocarbon fractions of solvent-refined coal by glass capillary gas chromatography/mass spectrometry. Fuel 58, 783-789.

Seifert W.K. (1977) Advances in Organic Geochemistry 1975 (eds. R. Campos and J. Goni) Enadimsa, p 21.

Seifert W.K. (1978) Steranes and terpanes in kerogen pyrolysis for correlation of oils and source rocks. Geochim. Cosmochim. Acta 42, 473-484.

Seifert W.K. and Moldowan J.M. (1978) Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Geochim. Cosmochim. Acta 42, 77-95.

Seifert W.K. and Moldowan J.M. (1979) The effect of biodegradation on steranes and terpanes in crude oils. Geochim. Cosmochim. Acta 43, 111-126.

Seifert W.K. and Moldowan J.M. (1980) The effect of thermal stress on source rock quality as measured by hopane stereochemistry. In Advances in Organic Geochemistry 1979 (Physics and Chemistry of the Earth Vol. 12) (eds. A.G. Douglas and J.R. Maxwell), p 229-237. Pergamon Press.

Selucky M.L., Chu Y., Ruo T. and Strausz O.P. (1977) Chemical composition of Athabasca bitumen. Fuel 56, 369-380.

Shaw G.J., Quirke J.M.E. and Eglinton G. (1978) Analysis of petroporphyrins by chemical ionisation mass spectrometry. J. Chem. Soc. Perkin Trans. 1, 1655-1659.

Simoneit B.R. and Burlingame A.L. (1973) Carboxylic acids derived from Tasmanite by extraction and kerogen oxidation. Geochim. Cosmochim. Acta 37, 595-610.

Simoneit B.R. (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acta 41, 463-476.

Simoneit B.R. (1978) The organic chemistry of marine sediments. In Chemical Oceanography (eds. J.P. Riley and R. Chester), Vol. 7, 2nd edn., p 233-311. Academic Press.

Smith J.R., Smith C.R. and Dinneen G.U. (1950) Separation of nitrogen compounds by adsorption from shale oil. Anal. Chem. 22, 867-870.

Snyder L.R. and Roth W.F. (1964) Routine separation and determination of total saturated hydrocarbons in heavy petroleum samples by adsorption chromatography. Anal. Chem. 36, 128-131.

Snyder L.R. (1966) Qualitative analysis of petroleum and related materials using linear elution adsorption chromatography. Anal. Chem. 38, 1319-1323.

Snyder L.R. and Schunk T.C. (1982) Retention mechanism and the role of the mobile phase in normal phase separation on amino-bonded-phase columns. Anal. Chem. 54, 1764-1772.

Solomons T.W.G. (1976) Organic Chemistry p 165, John Wiley, New York.

Southern Pacific Petroleum NL (1981) Annual Report.

Spyckerelle C., Greiner A.C., Albrecht P. and Ourisson G. (1977a) Aromatic hydrocarbons from geological sources. III. A tetrahydrochrysene derived from triterpenes in Recent and old sediments: 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene. J. Chem. Res. (M), 1977, 3746-3777; (S), 1977, 330-331.

Spyckerelle C., Greiner A.C., Albrecht P. and Ourisson G. (1977b) Aromatic hydrocarbons from geological sources. IV. An octahydrochrysene derived from triterpenes in oil shale: 3,3,7,12a-tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene. J. Chem. Res. (M), 1977, 3801-3828; (S), 1977, 332-333.

Stanfield K.E. and Frost I.C. (1949) Report of investigation 4477 US Bureau of Mines, Washington, DC.

Steel G. and Henderson W. (1972) Isolation and characterization of stanols from the Green River shale. Nature 238, 148-149.

Stenhagen E., Abrahamsson S. and McLafferty F.W. (1974) Registry of mass spectral data. Wiley, New York.

Streibl M. and Herout V. (1969) Terpenoids - Especially oxygenated mono, sesqui-, di- and triterpenes. In Organic Geochemistry (eds. G. Eglinton and M.T.J. Murphy) p 401-424, Springer-Verlag.

Sykes P. (1967) A Guidebook to Mechanism in Organic Chemistry 2nd edn. p 236, Longmans, London.

Tissot B.P. and Welte D.H. (1978a) Petroleum Formation and Occurrence p 147, Springer-Verlag.

Tissot B.P. and Welte D.H. (1978b) Petroleum Formation and Occurrence p 109, Springer-Verlag.

Tissot B.P. and Welte D.H. (1978c) Petroleum Formation and Occurrence p 44, Springer-Verlag.

Treibs A. (1936) Chlorophyll and hemin derivatives in organic materials. Angew. Chem. 49, 628-686.

Turner A.C. (1965) Oil shale. Australian mineral industry: the mineral deposits. Bureau of Mineral Resources, Australia. Bulletin 72, 459-466.

Uden P.C., Carpenter A.P., Hackett H.M., Henderson D.E. and Siggia S. (1979) Qualitative analysis of shale oil acids and bases by porous layer open tubular gas chromatography and interfaced vapour phase infrared spectrophotometry. Anal. Chem. 51, 38-43.

Van Dorsselaer A., Ensminger A., Spyckerelle C., Dastillung M., Sieskind O., Arpino P., Albrecht P., Ourisson G., Brooks P.W., Gaskell G.J., Kimble B.J., Philp R.P., Maxwell J.R. and Eglinton G. (1974) Degraded and extended hopane derivatives (C_{27} to C_{35}) as ubiquitous geochemical markers. Tetrahedron Lett. 1349-1352.

Van Krevelen D.W. (1981) Coal Elsevier.

Van Vleet E.S. and Quinn J.G. (1976) Characterization of monounsaturated fatty acids from an estuarine sediment Nature, 262, 126-128.

Vitorovic D.K. and Pfendt P.A. (1967) Investigation of the kerogen of a Yugoslav (Aleksinac) oil shale. Proc. 7th World Pet. Congr. 3, 691-694.

Vitorovic D., Djuricic M.V. and Ilic B. (1974) New structural information obtained by stepwise oxidation of kerogen from the Aleksinac (Yugoslavia) shale. In Advances in Organic Geochemistry 1973 (eds. B. Tissot and F. Bienner), p 179-189. Technip.

Vitorovic D., Vucelic D., Gasic M.J., Juranic N. and Mariva S. (1978) Analysis of the organic matter of oil shales by nuclear magnetic resonance Org. Geochem. 1, 89-91.

Wakeham S.G., Schaffner C. and Giger W. (1980a) Polycyclic aromatic hydrocarbons in Recent lake sediments. II. Compounds derived from biogenic precursors during early diagenesis. Geochim. Cosmochim. Acta 44, 415-429.

Wakeham S.G., Schaffner C. and Giger W. (1980b) Diagenetic polycyclic aromatic hydrocarbons in Recent sediments: Structural information obtained by high performance liquid chromatography. In Advances in Organic Geochemistry 1979 (Physics and Chemistry of the Earth Vol. 12) (eds. A.G. Douglas and J.R. Maxwell), p 353-363. Pergamon Press.

Wardroper A.M.K., Brooks P.W., Humberston M.J. and Maxwell J.R. (1977) Analysis of steranes and triterpanes in geolipid extracts by automatic classification of mass spectra. Geochim. Cosmochim. Acta 41, 499-510.

Weast R.C. (1980) Handbook of Chemistry and Physics. p 2216. C.R.C. Press, Cleveland.

Wilson B.W., Petersen M.R., Pelroy R.A. and Cresto J.T. (1981) In-vitro assay for mutagenic activity and gas chromatographic-mass spectral analysis of coal liquefaction material and the products resulting from its hydrogenation. Fuel 60, 289-294.

Wise S.A., Chesler S.N., Hertz H.S., Hilpert L.R. and May W.E. (1977) Chemically-bonded aminosilane stationary phase for the high-performance liquid chromatographic separation of polynuclear aromatic compounds. Anal. Chem. 49, 2306-2310.

Wollrab V. and Streibl M. (1969) Earth waxes, peat, montan wax and other organic brown coal constituents. In Organic Geochemistry (eds. G. Eglinton and M.T.J. Murphy) Chap. 24, p 576-598. Springer-Verlag.

Wszolek P.C., Gelpi E. and Burlingame A.L. (1972) A new approach to the isolation of milligram amounts of significant geochemical compounds. In Advances in Organic Geochemistry 1971 (eds. H.R. Gaertner and H. Wehner), p 229-247. Pergamon Press.

Yen T.F. and Chilingarian G.V. (1976) Introduction to oil shales. In Developments in Petroleum Science, 5. Oil Shale (eds. T.F. Yen and G.V. Chilingarian), p 1-12. Elsevier.

A P P E N D I X

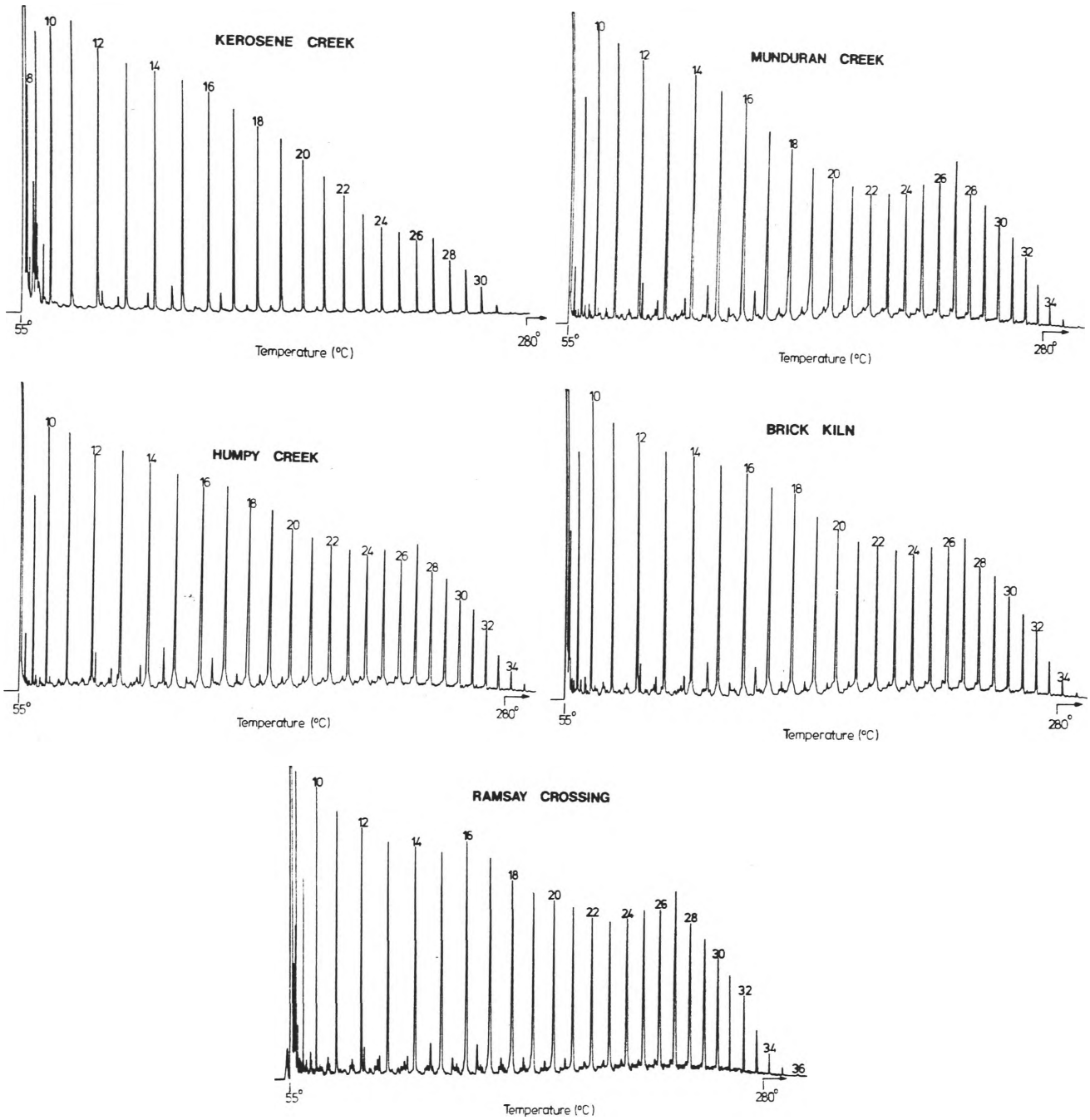

Figure A. Gas chromatograms of the total alkane fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Carbon numbers of homologous linear alkanes are indicated.

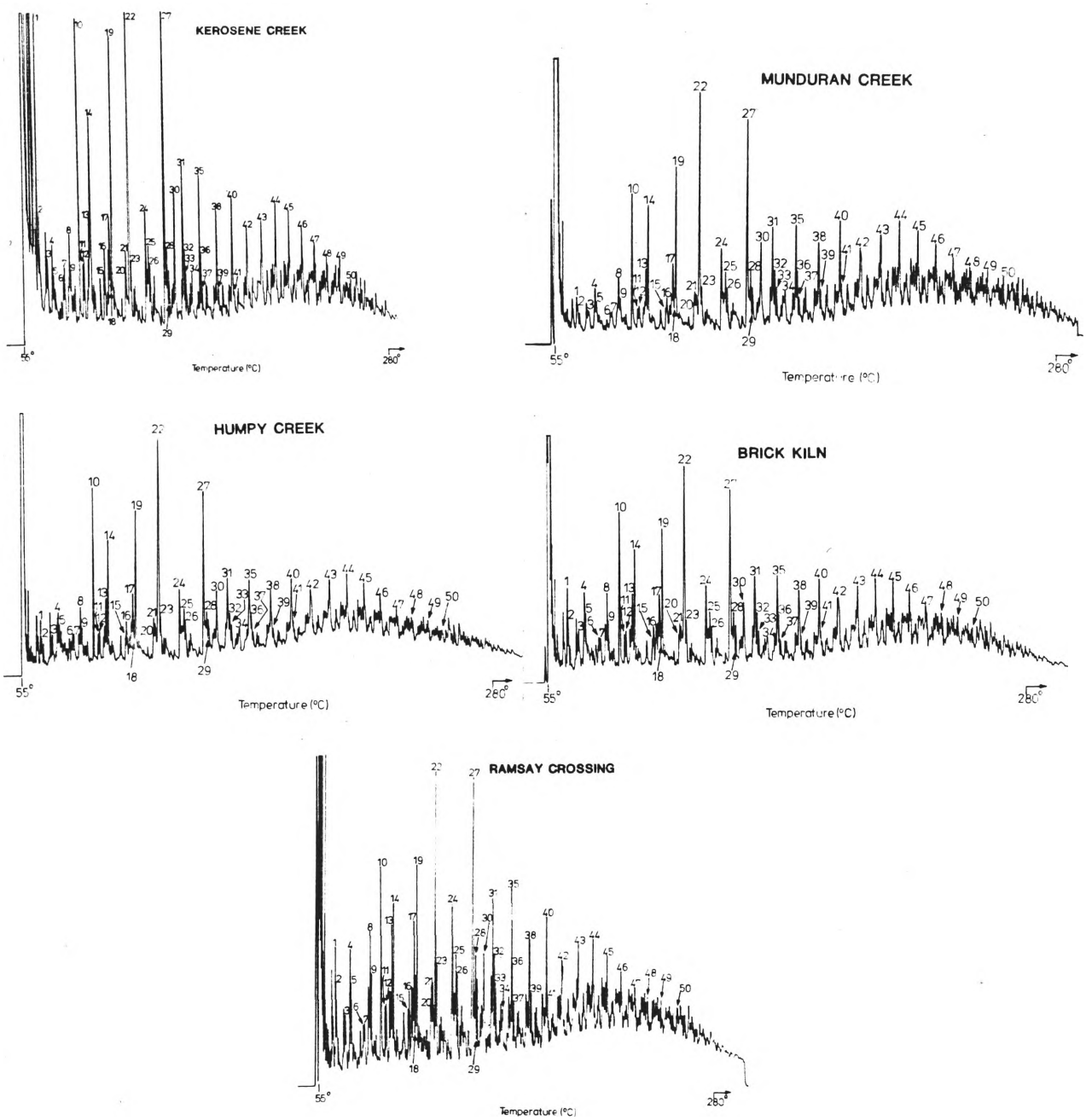

Figure B. Gas chromatograms of the branched/cyclic alkane fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Numbers refer to compounds in Table 5.

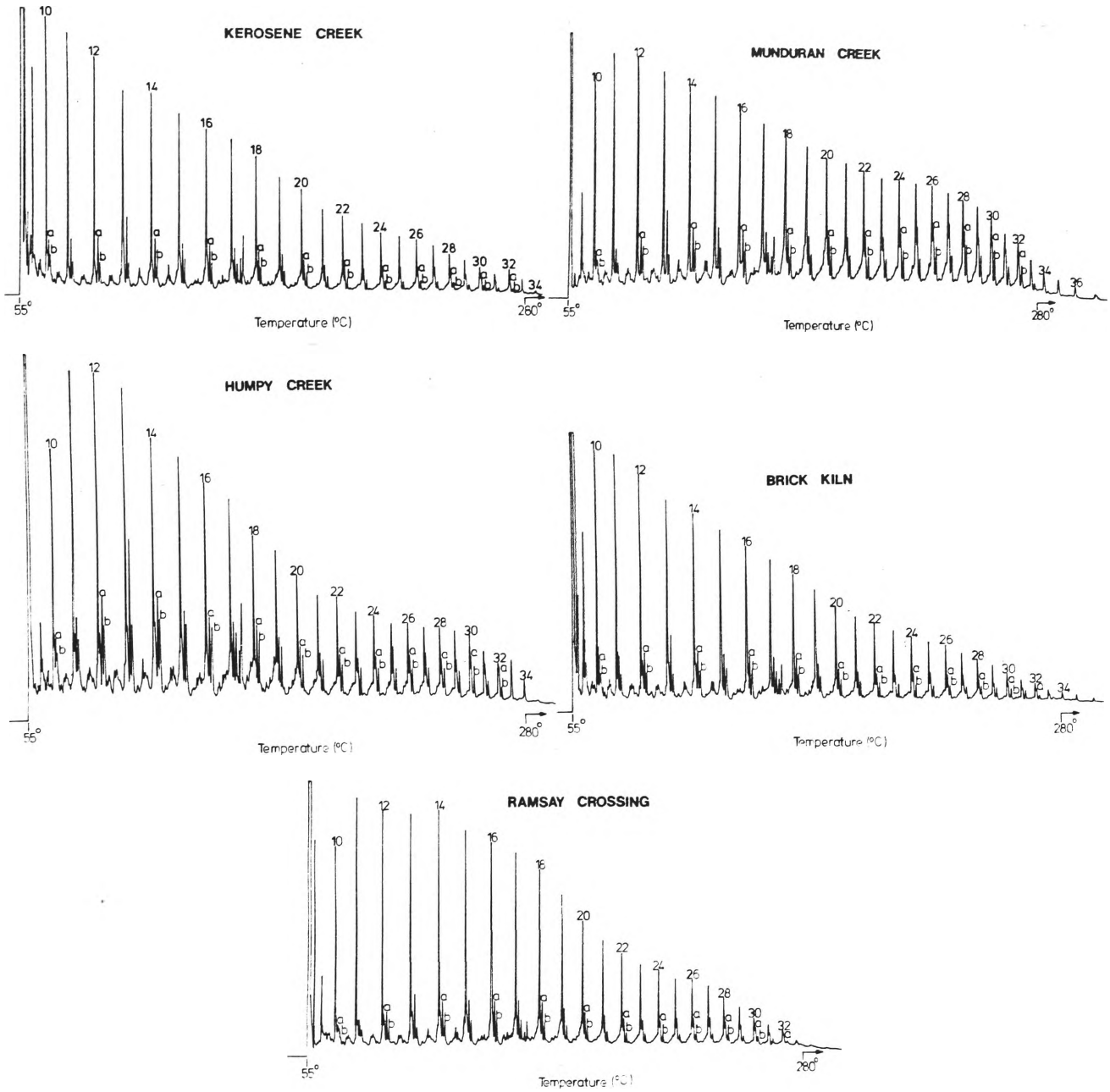

Figure C. Gas chromatograms of the total alkene fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Carbon numbers of homologous 1-alkenes are indicated. a and b denote homologous 3- and 2-alkenes respectively.

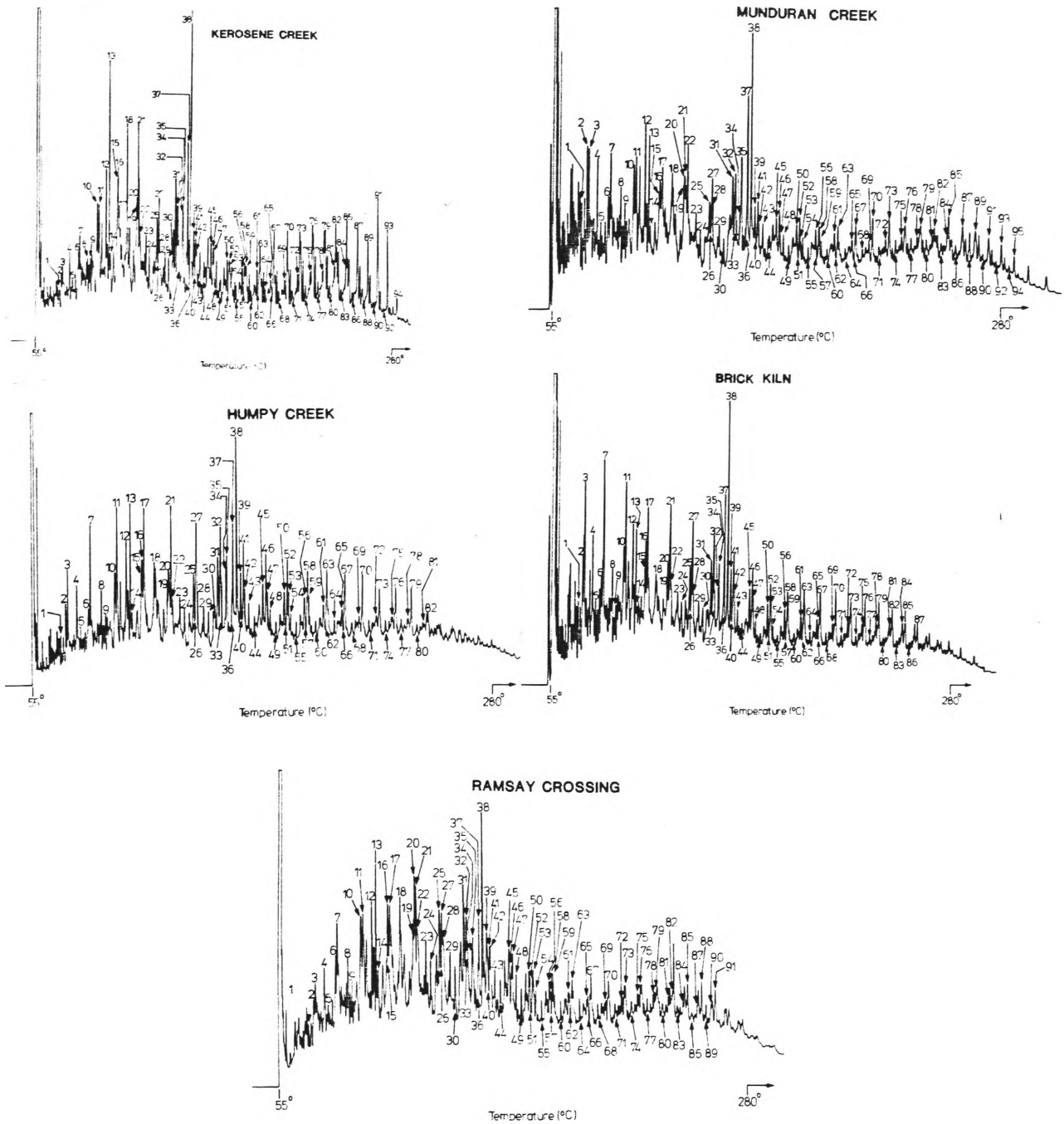

Figure D. Gas chromatograms of the branched/cyclic alkene/alkylbenzene fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Numbers refer to compounds in Table 6.

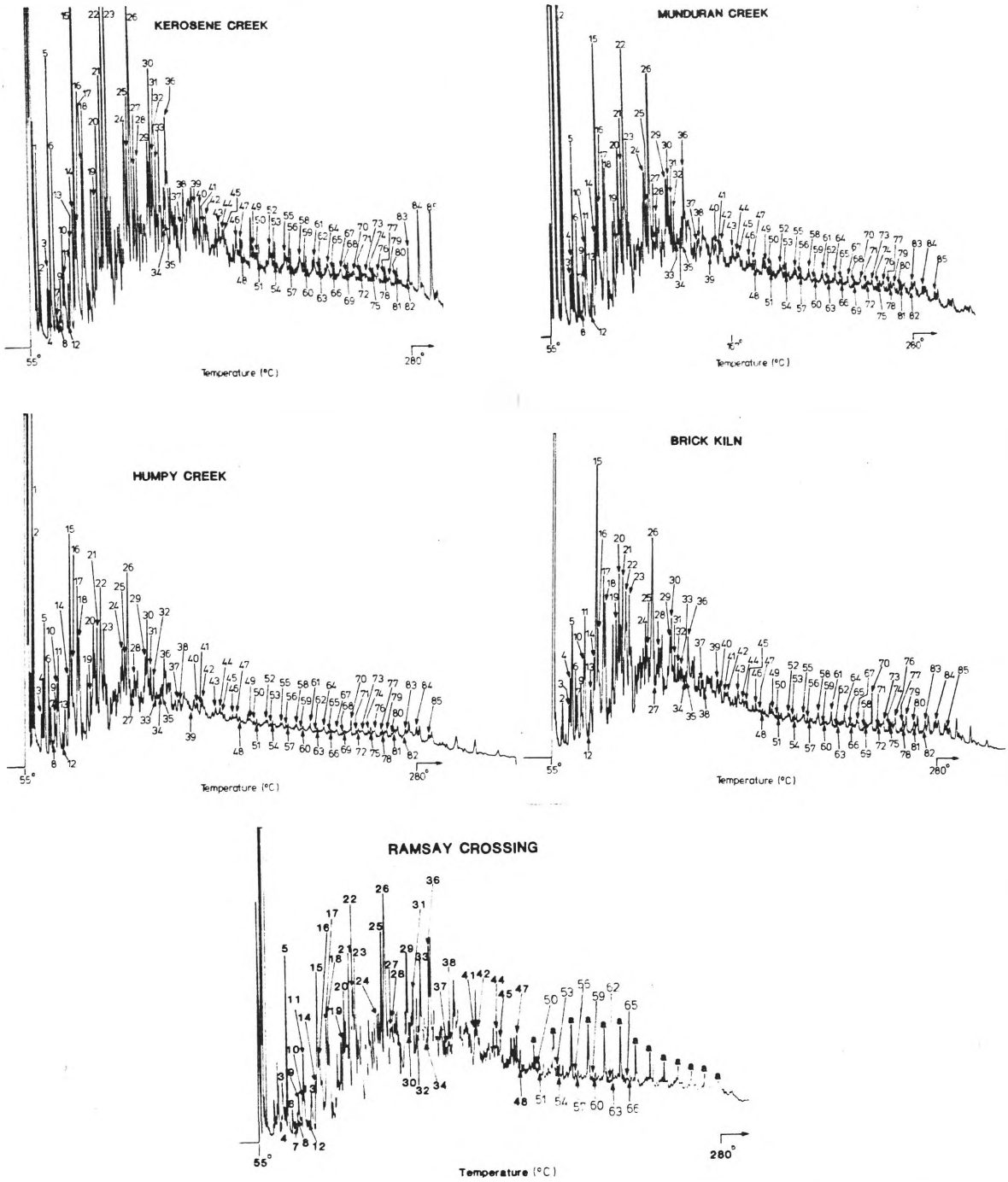

Figure E. Gas chromatograms of the diaromatic fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Numbers refer to compounds in Table 7.

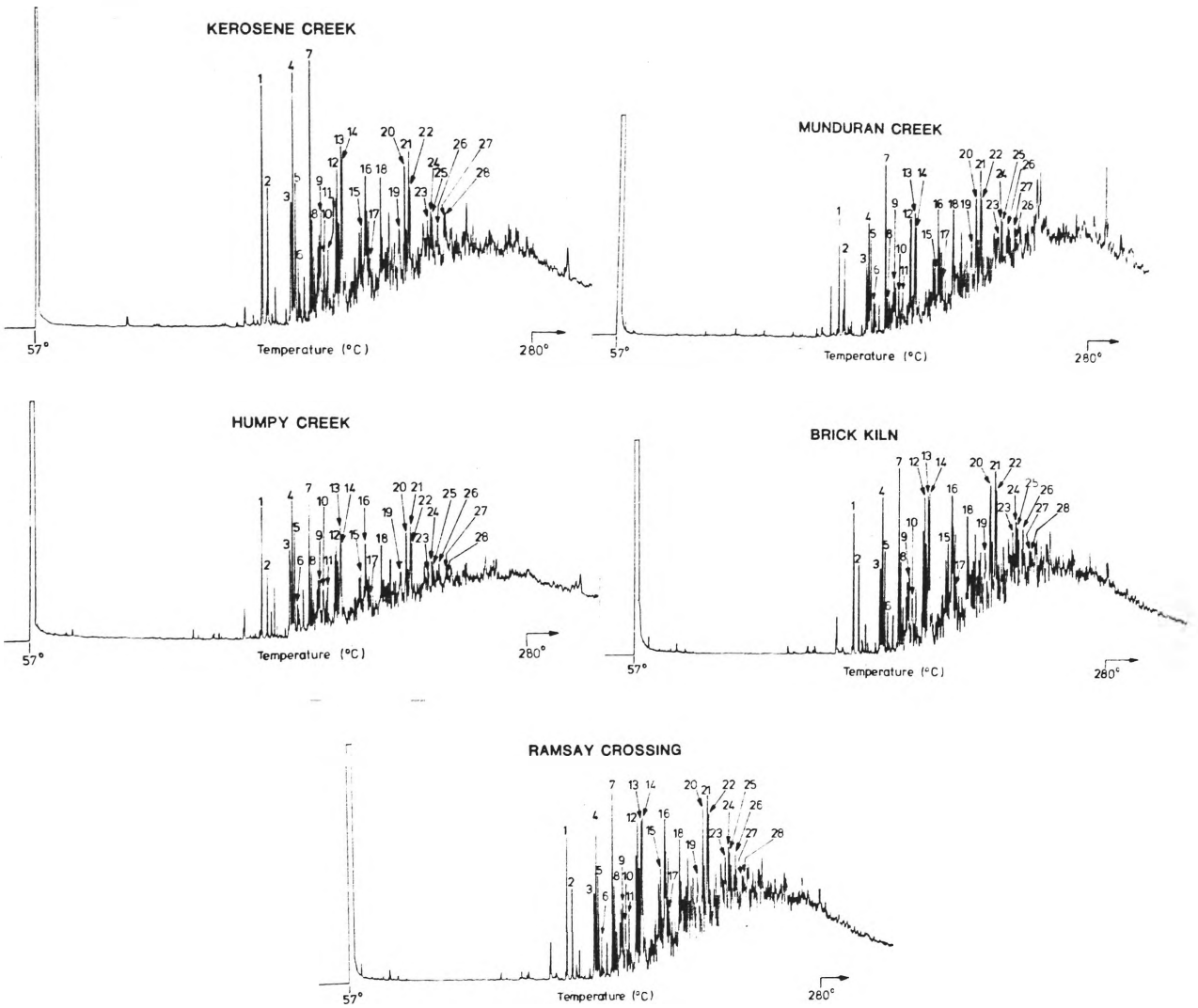

Figure F. Gas chromatograms of the polyaromatic fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Numbers refer to compounds in Table 8.

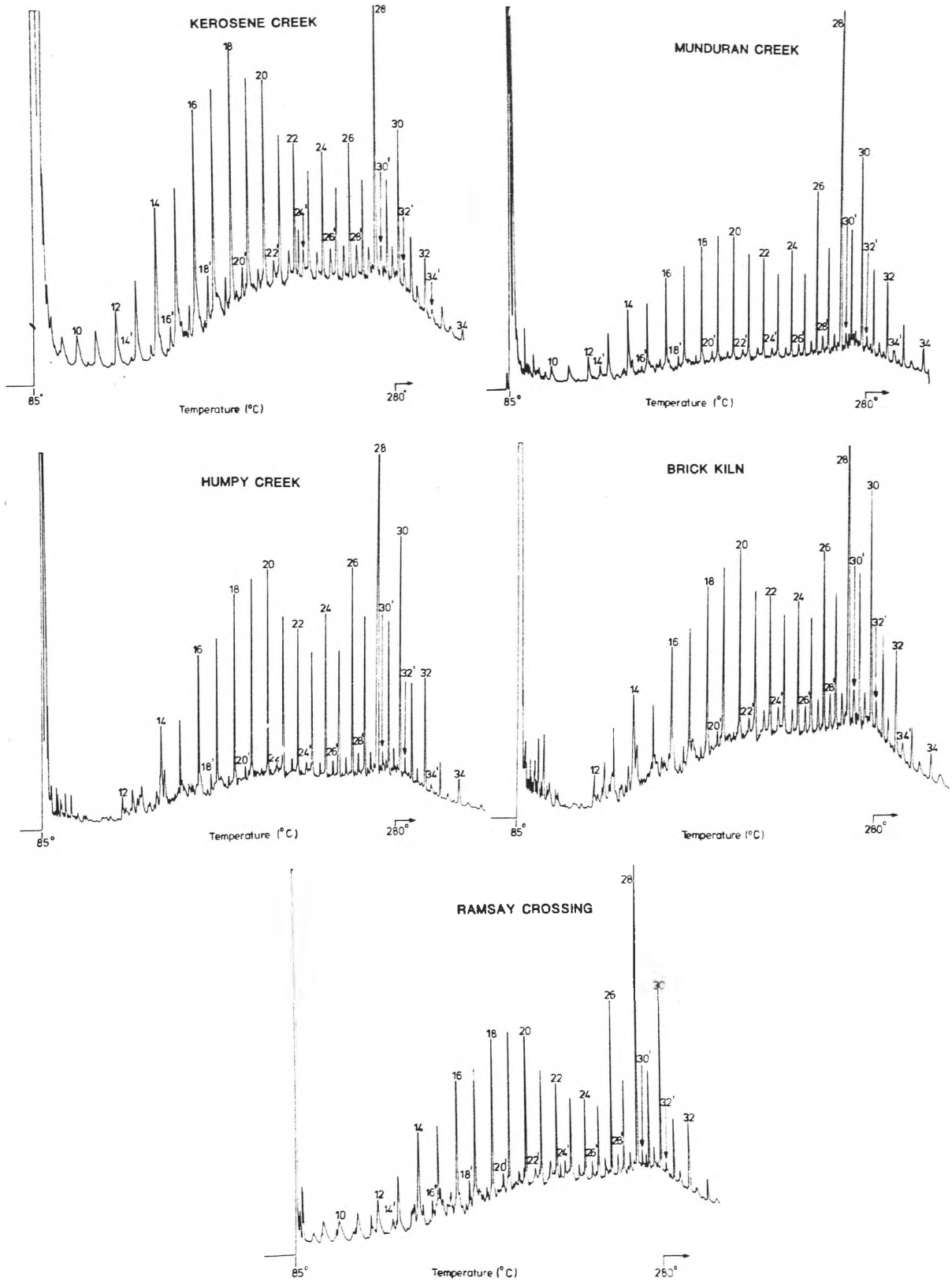

Figure G. Gas chromatograms of the nitrile fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Carbon numbers are indicated for homologous straight-chain alkylnitriles (no prime) and 6-alkanones (with prime).

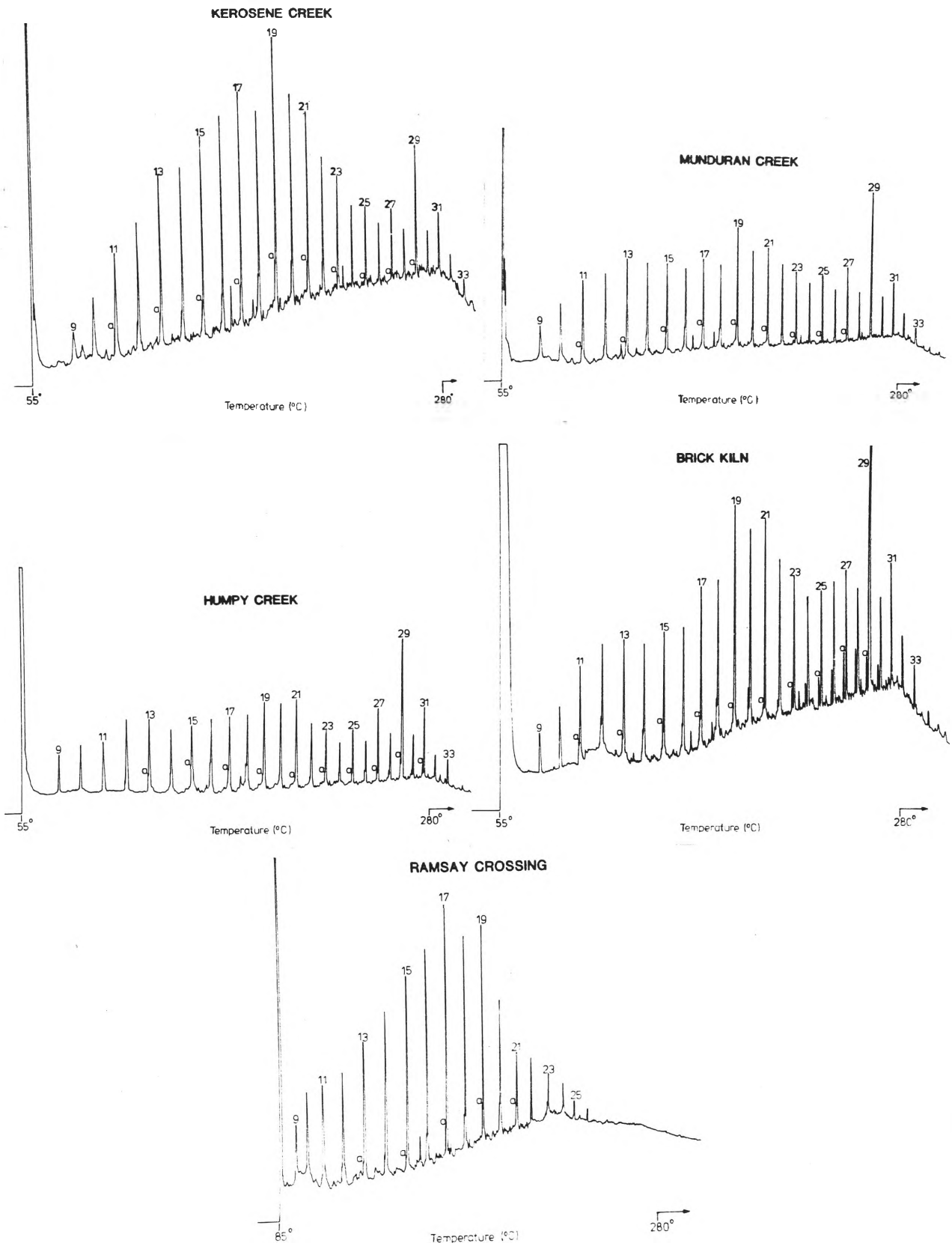

Figure H. Gas chromatograms of the methyl ketone fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Carbon numbers of homologous 2-alkanones are indicated. a denotes a series of homologous unsaturated straight-chain methyl ketones.

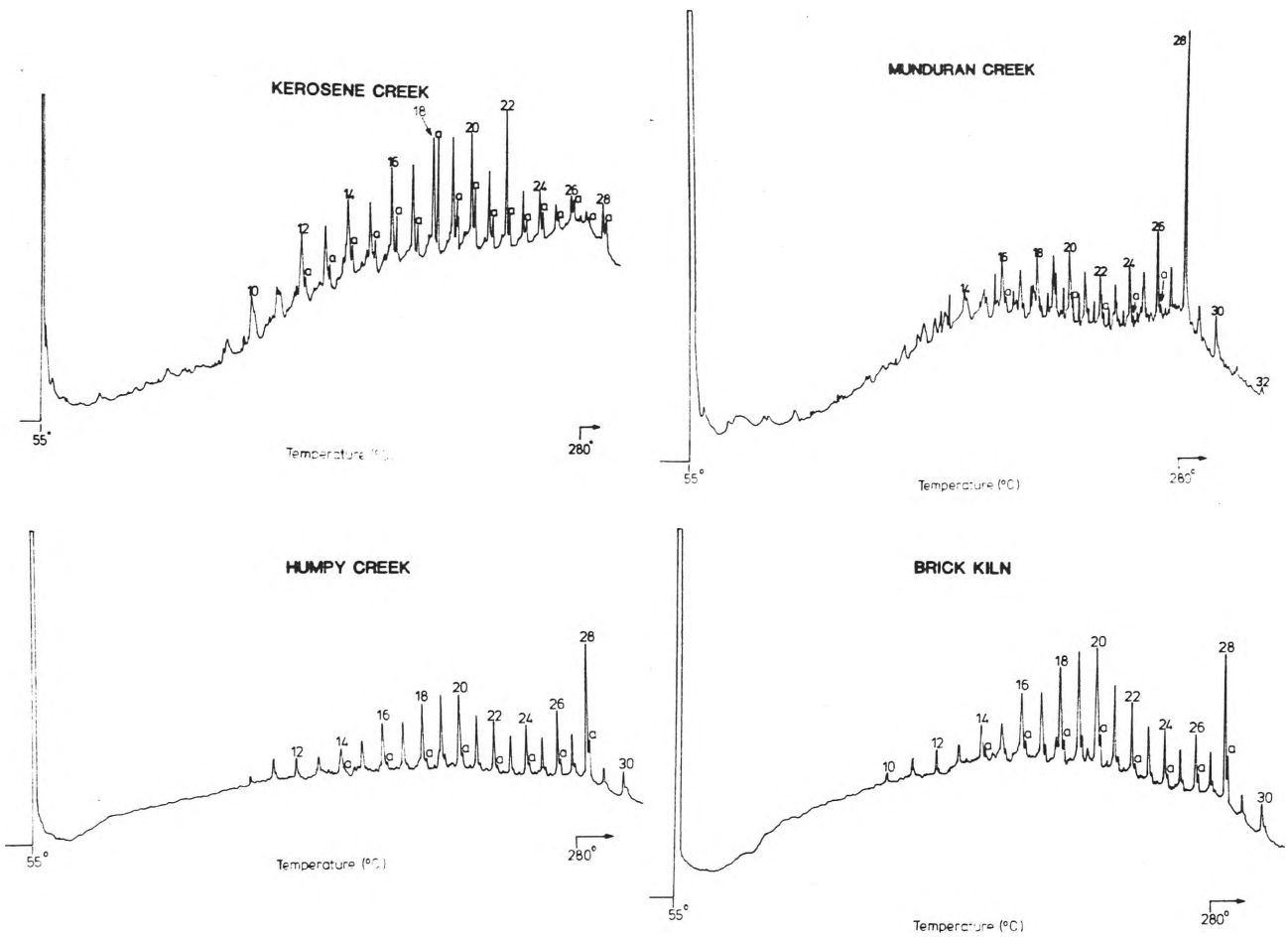

Figure I. Gas chromatograms of the amide fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Carbon numbers of homologous straight-chain alkanamides are indicated. a denotes a series of homologous 2-methylalkanamides.

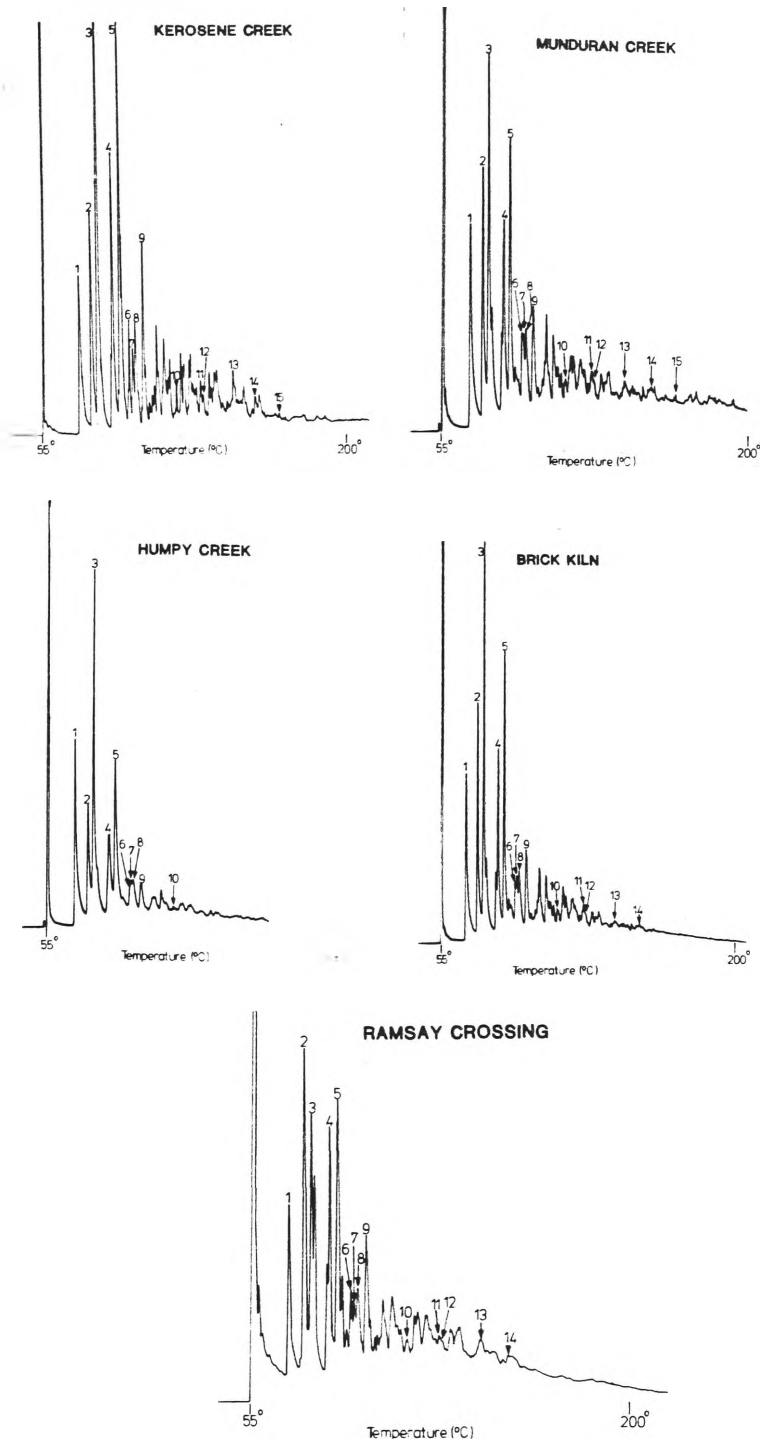

Figure J. Gas chromatograms of the phenolic (acidic) fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Numbers refer to compounds in Table 9.

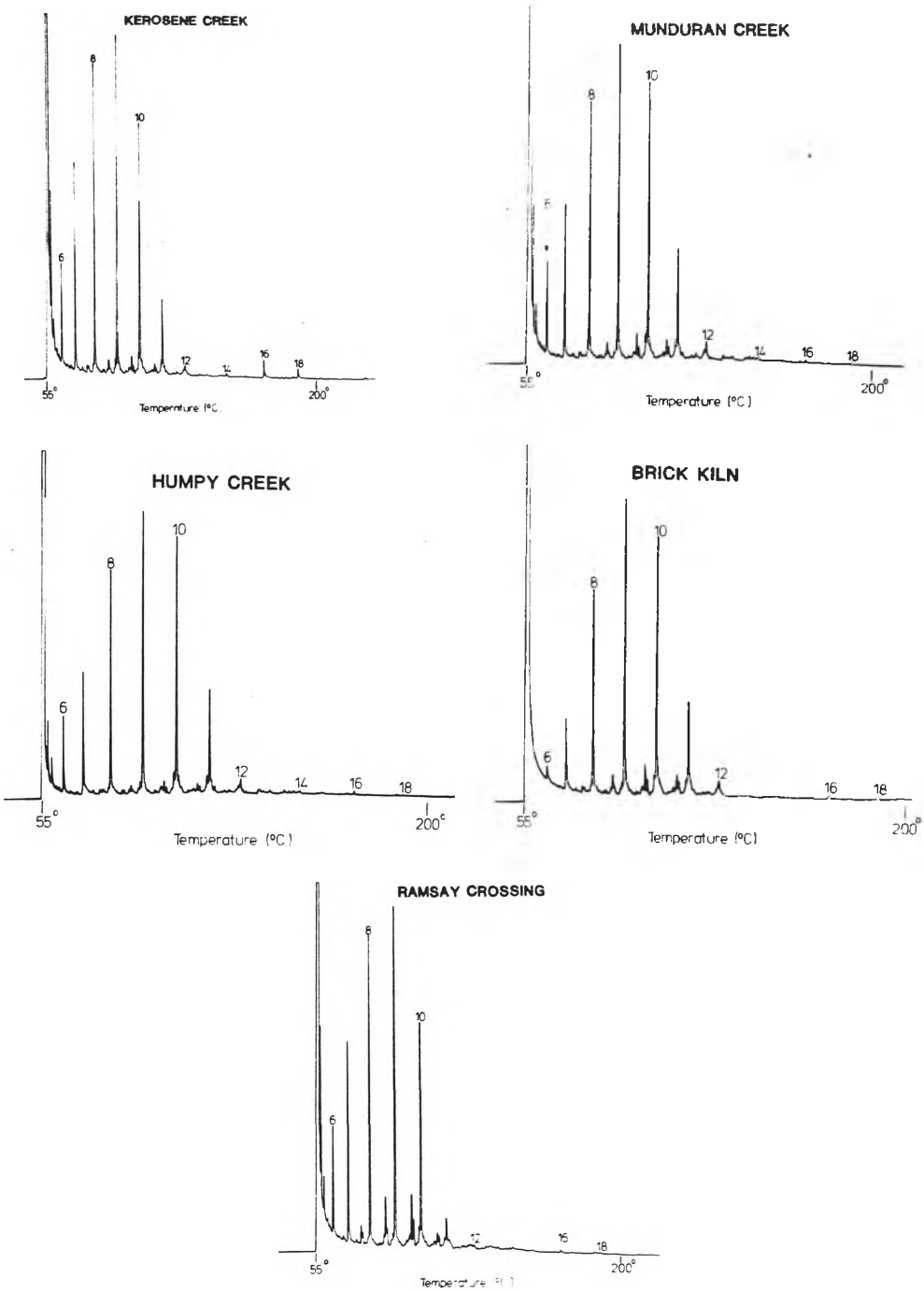

Figure K. Gas chromatograms of the methyl ester derivatives of aliphatic carboxylic acids from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Carbon numbers are indicated.

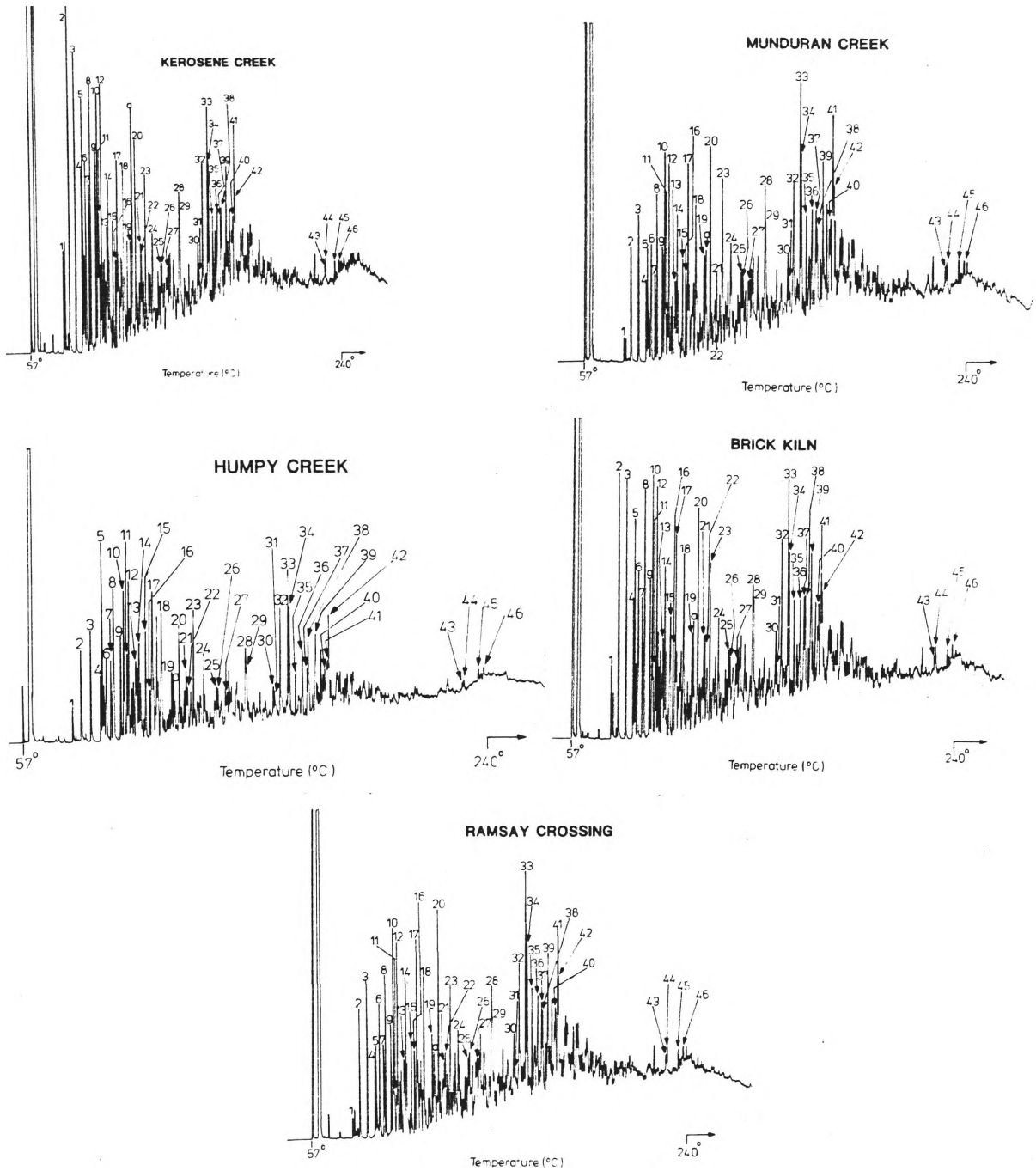

Figure L. Gas chromatograms of the basic fractions from the Fischer Assay oils extracted from various stratigraphic levels of the Rundle deposit. Numbers refer to compounds in Table 10.